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(54) Title: SPECIES MODIFICATION IN MACROCYCLIC POLYESTER OLIGOMERS, AND COMPOSITIONS PREPARED THEREBY

(57) Abstract: Physical properties, such as melting temperature of MPO compositions may be significantly modified by modifying the weight percentage of one or more of the constituent MPOs. For example, removal of a significant portion of the tetramer can afford low melting MPO compositions. In one aspect, the invention is related to a method for modifying a physical property of a MPO composition that includes the steps of (a) providing a composition that has at least two species of MPOs, and (b) changing the weight percentage of at least one species of the MPOs in the composition. In another aspect, the invention is related to a MPO composition that includes at least two species of MPOs where a species of the MPOs having the highest melting temperature is present in an amount less than or equal to 5 %. In yet another aspect, the invention is related to a MPO composition comprising 30-40 % macrocyclic polyester dimers, 30-45 % macrocyclic polyester trimers, 0-5 % macrocyclic polyester tetramers, and 5-20 % macrocyclic polyester pentamers.

WO 02/22738 A2

SPECIES MODIFICATION IN MACROCYCLIC POLYESTER OLIGOMERS, AND COMPOSITIONS PREPARED THEREBY

Technical Field

This invention generally relates to thermoplastics and articles formed therefrom. More particularly, the invention relates to macrocyclic polyester oligomer compositions and methods for modifying physical and chemical properties of the compositions. Even more particularly, this invention relates to macrocyclic polyester oligomer compositions having relatively low melting
5 temperatures.

Background Information

Linear polyesters such as poly(alkylene terephthalate) are generally known and commercially available where the alkylene typically has 2 to 8 carbon atoms. Linear polyesters have many valuable characteristics including strength, toughness, high gloss and solvent
10 resistance. Linear polyesters are conventionally prepared by the reaction of a diol with a dicarboxylic acid or its functional derivative, typically a diacid halide or ester. Linear polyesters may be fabricated into articles of manufacture by a number of known techniques including extrusion, compression molding, and injection molding. Linear polyesters may be produced from macrocyclic polyester oligomers.

15 Macrocyclic polyester oligomers (MPOs) have unique properties that make them attractive as matrices for engineering thermoplastic composites. These desirable properties stem from the fact that MPOs exhibit low melt viscosity, allowing them to impregnate a dense fibrous preform easily. Furthermore, certain MPOs melt and polymerize at temperatures well below the melting point of the resulting polymer. Upon melting and in the presence of an appropriate
20 catalyst, polymerization and crystallization can occur virtually isothermally. As a result, the time and expense required to thermally cycle a tool is favorably reduced.

 Generally speaking, MPO compositions have high melting temperatures, which necessitate the use of special equipment in processing not commonly available in polymer processing units. If compositions with lower melting temperatures could be produced, it would
25 be possible to use more readily available processing equipment such as that is commonly used in the production and handling of epoxy resins.

- 2 -

Summary of the Invention

Physical and/or chemical properties of MPO compositions may be significantly modified by modifying the weight percentage of one or more of the constituent MPOs. For example, the presence of a single MPO species, the macrocyclic polyester tetramer, has an unexpectedly pronounced effect on the melting temperature of a MPO composition. Removal of a portion of the macrocyclic polyester tetramer can result in low-melting MPO compositions. The resulting MPO compositions have the further advantage, under many circumstances, of a greatly reduced tendency to crystallize at ambient temperatures, making it possible to combine them with fillers such as carbon or glass fibers to produce prepregs easily convertible to filled high molecular weight linear polyesters.

In one aspect, the invention is related to a process for modifying a physical property of a composition that includes MPOs. The process includes the steps of (a) providing a composition that has at least two species of MPOs, and (b) changing the weight percentage of at least one species of the MPOs in the composition.

In another aspect, the invention is related to a MPO composition that includes at least two species of MPOs wherein a species of the MPOs having the highest melting temperature is present in an amount less than or equal to 5%. In one embodiment, a blend material includes such a MPO composition and also a polymerization catalyst.

In a preferred embodiment, a MPO composition of the invention comprises 30-40% macrocyclic polyester dimers, 30-45% macrocyclic polyester trimers, 0-5% macrocyclic polyester tetramers, and 5-20% macrocyclic polyester pentamers.

The foregoing and other objects, aspects, features, and advantages of the invention will become more apparent from the following figures, description, and claims.

Brief Description of Figures

The drawings are not necessarily to scale, emphasis instead being generally placed upon illustrating the principles of the invention to facilitate its understanding.

FIG. 1 is a schematic illustration of an embodiment of the invention including a fractional crystallization process.

Detailed Description

Physical properties, for example, the melting temperatures, of a composition comprising MPOs may be modified by modifying the weight percentage of a MPO species, for example, the macrocyclic polyester tetramer. A MPO composition having a low melting temperature can be

- 3 -

polymerized and processed at lower temperature thereby avoiding the need for special equipment not commonly available in polymer processing.

Definitions

5 The following general definitions may be helpful in understanding the various terms and expressions used in this specification.

As used herein, "macrocyclic" means a cyclic molecule having at least one ring within its molecular structure that contains 8 or more atoms covalently connected to form the ring.

As used herein, an "oligomer" means a molecule that contains 2 or more identifiable structural repeat units of the same or different formula.

10 As used herein, a "macrocyclic polyester oligomer (MPO)" means a macrocyclic oligomer containing structural repeat units having an ester functionality. A MPO typically refers to multiple molecules of one specific formula. However, a MPO also may include multiple molecules of different formulae having varying numbers of the same or different structural repeat units. In addition, a MPO may be a macrocyclic co-polyester oligomer (including macrocyclic
15 multi-polyester oligomer), i.e., an oligomer having two or more different structural repeat units having an ester functionality within one cyclic molecule.

As used herein, "degree of polymerization (DP)" means the number of identifiable structural repeat units in oligomeric or polymeric backbone. The structural repeat units may have the same or different molecular structural. For example, "macrocyclic polyester tetramer" or
20 "tetramer" refers to MPOs with a DP of 4.

As used herein, a "species" means MPOs having the same DP. For example, the macrocyclic polyester tetramer is one species.

As used herein, a "macrocyclic polyester oligomer composition" means a composition comprising a mixture of MPOs having different DP values, whether or not units of more than one
25 molecular structure are present.

As used herein, a "blend material" means a mixture of two or more components including at least one MPO and at least one polymerization catalyst. Preferably the blend material is uniformly mixed. A blend material may also include a filler as well as other components recognized by a skilled artisan.

30 As used herein, "substantially homo- or co-polyester oligomer" means a polyester oligomer wherein the structural repeat units are substantially identical or substantially two different structural repeat units, respectively.

As used herein, "an alkylene group" means $-C_nH_{2n}-$, where $n \geq 2$.

- 4 -

As used herein, "a cycloalkylene group" means a cyclic alkylene group, $-C_nH_{2n-x}-$, where x represents the number of H's replaced by cyclization(s).

As used herein, "a mono- or polyoxyalkylene group" means $[-(CH_2)_m-O-]_n-(CH_2)_m-$, wherein m is an integer greater than 1 and n is an integer greater than 0.

5 As used herein, "a divalent aromatic group" means an aromatic group with links to other parts of the macrocyclic molecule. For example, a divalent aromatic group may include a meta- or para- linked monocyclic aromatic group (e.g., benzene).

As used herein, "an alicyclic group" means a non-aromatic hydrocarbon group containing a cyclic structure within.

10 As used herein, "a filler" means a material other than a MPO or a polymerization catalyst that may be included in the blend material. A filler often is included to achieve a desired purpose or property, and may be present in the resulting polyester polymer. For example, the purpose of the filler may be to provide stability, such as chemical, thermal or light stability, to the blend material or the polyester polymer product, and/or to increase the strength of the polyester
15 polymer product. A filler also may provide or reduce color, provide weight or bulk to achieve a particular density, provide flame resistance (i.e., be a flame retardant), be a substitute for a more expensive material, facilitate processing, and/or provide other desirable properties as recognized by a skilled artisan. Illustrative examples of fillers are, among others, fumed silica, carbon black, titanium dioxide, organo bromides in combination with antimony oxides, calcium carbonate,
20 chopped fibers, fly ash, glass microspheres, micro-balloons, crushed stone, nanoclay, linear polymers, and monomers.

As used herein, "a polyester polymer composite" means a polyester polymer that is associated with another substrate such as, a fibrous or particulate material. Illustrative examples of particulate materials are chopped fibers, glass microspheres, and crushed stone.

25 As used herein, "an equilibrated mixture" means a mixture of MPOs in thermodynamic or kinetic equilibration.

As used herein, "fiber" means any material with elongated structure such as polymer or natural fibers. The material can be fiberglass, ceramic fibers, carbon fibers or organic polymers such as aramid fibers.

30 As used herein, a "tow" or "strand" means a group of fibers together, or a bundle of fibers, which are usually wound onto spools and may or may not be twisted. These tows or strands can be woven or knitted to form fabrics.

- 5 -

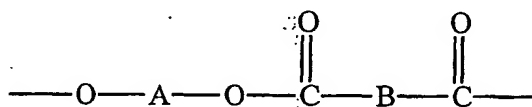
As used herein, a "fiber preform" means an assembly of fiber tows and/or fabric held together in a desired shape. Typically, fiber preforms are dry, and often held together with various tackifiers.

As used herein, a "prepreg" means a fiber material such as carbon fiber, glass fiber, or other fiber, that has been impregnated with a resin material in sufficient volume as to provide the matrix of the composite, and such that the ratio of fiber to resin is closely controlled. The fiber configuration can be in tow form, woven or knitted into a fabric, or in a unidirectional tape.

I. Macrocylic Polyester Oligomers (MPOs)

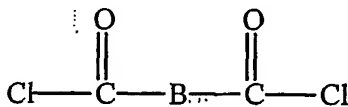
Many different MPOs can readily be made and are useful in the practice of this invention.

MPOs that may be employed in this invention include, but are not limited to, macrocyclic poly(alkylene dicarboxylate) oligomers having a structural repeat unit of the formula:



where A is an alkylene, or a cycloalkylene or a mono- or polyoxyalkylene group; and B is a divalent aromatic or alicyclic group. MPOs that may be employed in this invention may have various DP values, e.g., 2 to 20, 2 to 10, 2 to 8, and 2 to 6.

MPOs may be prepared by known methods. Synthesis of the preferred MPOs may include the step of contacting at least one diol of the formula HO-A-OH with at least one diacid chloride of the formula:



where A and B are as defined above. The reaction typically is conducted in the presence of at least one amine that has substantially no steric hindrance around the basic nitrogen atom. An illustrative example of such an amine is 1,4-diazabicyclo[2.2.2]octane (DABCO). The reaction usually is conducted under substantially anhydrous conditions in a substantially water immiscible organic solvent such as methylene chloride. The temperature of the reaction typically is between about -25°C and about 25°C. See, e.g., U.S. Patent No. 5,039,783 to Brunelle *et al.*

MPOs have also been prepared via the condensation of a diacid chloride with at least one bis(hydroxyalkyl) ester such as bis(4-hydroxybutyl) terephthalate. The condensation typically occurs in the presence of a highly unhindered amine or a mixture thereof with at least one other

- 6 -

tertiary amine such as triethylamine. Usually, a substantially inert organic solvent such as methylene chloride, chlorobenzene, or a mixture thereof is used. See, e.g., U.S. Patent No. 5,231,161 to Brunelle *et al.*

Another method for preparing MPOs, including macrocyclic co-polyester oligomers, is to depolymerize linear polyester polymers in the presence of an organotin or titanate compound. In this method, linear polyesters are converted to MPOs by heating a mixture of linear polyesters, an organic solvent, and a trans-esterification catalyst such as a tin or titanium compound. The solvents used, such as *o*-xylene and *o*-dichlorobenzene, usually are substantially free of oxygen and water. See, e.g., U.S. Patent Nos. 5,407,984 to Brunelle *et al.* and 5,668,186 to Brunelle *et al.*

It is also within the scope of the invention to employ macrocyclic homo- and co-polyester oligomers to produce homo- and co-polyester polymers, respectively. Therefore, unless otherwise stated, an embodiment of a composition, article, or process that refers to a MPO may also include co-polyester embodiments.

Among homopolymeric compositions and in one embodiment, MPOs of poly(1,4-butylene) terephthalate (PBT) are used. Among homopolymeric compositions and in another embodiment, MPOs of polyethylene terephthalate (PET) are used. Among co-polymeric compositions and in one embodiment, MPO species contain a major proportion of PBT structural units, PET structural units, or both. In one embodiment, MPO species contain at least about 90 mole percent of PBT structural units, PET structural units, or both. In another embodiment, MPO species contain predominately PBT, and a minor proportion of other units, for example, poly(alkylene dicarboxylate) units or ether oxygen-containing units such as those in which A is derived from diethylene glycol.

II. Designing Physical and Chemical Properties of MPO Compositions

In one embodiment, MPO compositions are created that have physical and/or chemical properties different from that of the unmodified MPO compositions originally produced. For example, the melting temperatures of a MPO composition can be significantly decreased by removal from the MPO composition of a major proportion of the macrocyclic polyester tetramer, i.e., the oligomer having a DP of 4. This is possible because the tetramer is both high melting and highly crystalline among the MPOs. Therefore, removal has a significant effect on the melting temperature and crystallinity of the oligomer composition. Similarly, the melting temperatures of a MPO composition can be significantly increased by adding into the MPO composition a significant proportion of the macrocyclic polyester tetramer.

- 7 -

In one aspect, the invention relates to a process for modifying a physical property of a composition having MPOs. The method includes the steps of (a) providing a composition having at least two species of MPOs, and (b) changing the weight percentage of at least one species of the MPOs in the composition. It should be understood that compositions may have three, four, or five or more species of MPOs present. In addition, although preferably the weight percentage of one species of the MPOs in the composition is changed, the invention contemplates changing more than one species in a composition.

In one embodiment, the physical property to be modified is the melting temperature of the composition. Besides melting temperature, other physical properties that may be modified by the method of the invention include, for example, crystallinity and viscosity. Modification of a selected physical property may be achieved by either increasing or reducing the weight percentage of at least one species of the MPOs in the composition.

In one embodiment, the weight percentage of at least the species having the highest melting temperature is reduced in step (b). In one embodiment, the weight percentage of at least macrocyclic polyester tetramer is reduced in step (b). In one embodiment, the MPO composition includes macrocyclic PBT oligomers. In another embodiment, the MPO composition includes macrocyclic PET oligomers. The MPO composition may contain homo-oligomer, co-oligomer, or both. In one embodiment, a MPO composition includes a macrocyclic co-polyester oligomer that has at least about 90% mole percent PBT structural units.

The proportion of macrocyclic polyester tetramer present in products prepared by reactions under thermodynamic control is generally greater than the proportion resulting from reactions under kinetic control. An example of a thermodynamically controlled reaction is depolymerization. The reaction of a diol with a dicarboxylic acid chloride is chiefly kinetically controlled.

In one embodiment, the proportion of macrocyclic polyester tetramer removed according to the invention is at least 60% by weight of the total amount of the macrocyclic polyester tetramer in the oligomer composition as originally prepared. The amount of macrocyclic polyester tetramer present can vary according to the method of preparation of the oligomer composition. In another embodiment, at least 70% of the macrocyclic polyester tetramer is removed. In yet another embodiment, at least 90% removal is performed.

In one embodiment, the reduction of the weight percentage of the macrocyclic polyester tetramer results in its weight percentage in the modified composition to be 60% less than its weight percentage in an equilibrated mixture of the MPOs according to the method of

preparation. In another embodiment, the weight percentage reduction is 70%. In yet another embodiment, the weight percentage reduction is 90%.

Any processes that result in modification of the weight percentage of a species of the MPOs may be employed. The effectiveness of such processes may be dependent on factors
5 including the nature of the original MPO composition and the particular species the proportion of which is to be modified. Illustrative examples of such processes include distillation, fractional crystallization, anti-solvent precipitation, addition and mixing, chemical reactions, etc.

In one embodiment, removal of a species of MPOs is achieved by fractional crystallization. In one embodiment, the macrocyclic polyester tetramer is removed by fractional
10 crystallization from a solution of the MPO composition. Any solvent that facilitates fractional crystallization may be employed. Illustrative suitable solvents include aromatic hydrocarbons and halogenated aromatic hydrocarbons, such as toluene, xylene and *o*-dichlorobenzene (ODCB). For example, in one embodiment, a 5% by weight solution of oligomer composition in ODCB at 110°C is cooled to ambient temperature of about 25°C, whereupon a precipitate forms that
15 contains a major proportion of the tetramer.

In one embodiment, removal of the macrocyclic polyester tetramer is achieved by anti-solvent precipitation. Illustrative suitable non-solvents include aliphatic hydrocarbons, especially those in the C₆₋₁₀ range such as hexane, heptane, octane and decane. In one preferred embodiment, heptane is used.

20 In one embodiment of a process of removing macrocyclic polyester tetramer by anti-solvent precipitation, the non-solvent is added to the MPO solution at an elevated temperature, in the range of about 80-120°C, after which the mixture is allowed to cool to a lower temperature, typically no higher than about 70°C since at lower temperatures substantial amounts of other oligomers, or the MPO composition in its entirety, may be precipitated. The amount of non-
25 solvent added is most often about 90-110% by volume of solvent used. Upon cooling to this lower temperature, a precipitate forms that is predominantly the macrocyclic polyester tetramer. A minor proportion of the macrocyclic polyester tetramer originally present usually remains in the MPO composition in solution. However, the remaining macrocyclic polyester tetramer does not have a significant effect on the melting temperature and crystallinity of the MPO
30 composition.

The MPO species removed may be reused for various purposes. In one embodiment, the MPO species, e.g., macrocyclic polyester tetramer, is polymerized separately or in combination with other MPOs or linears to produce linear polyester. In another embodiment, the MPO

- 9 -

species is equilibrated with linear polyester that is intended to be depolymerized, either before or during the depolymerization reaction. Depolymerization of a mixture of linear polyester and the MPO species removed from a MPO composition provides an oligomeric product that has the same distribution of oligomers as that obtained from linear polyester alone, showing that equilibration is essentially complete.

The apparatus for performing the above modification processes may be any conventional apparatus. The actual apparatus will depend on the actual process being employed. In one embodiment for performing fractional crystallization (referring to FIG. 1), an apparatus for producing the compositions of the invention may include a reactor vessel 110 in which the reaction constituents 120, e.g., linear polyester, solvent and depolymerization catalyst, are combined and the depolymerization reaction conducted. Subsequently, the product mixture passes through a filter 130 to remove linears. The filtrate may pass into a second vessel 140 where it is cooled to room temperature either in the presence or absence of aliphatic hydrocarbon as non-solvent to precipitate a species of MPO, e.g., the tetrameric species. The filtrate is then passed through another filter 150 which removes the precipitate, e.g., macrocyclic polyester tetramer. The precipitated macrocyclic polyester oligomers can be removed from the filter 150 and recycled to the reactor vessel 110. Further vessels may be employed downstream to isolate the product in the desired form and to remove non-solvent when it is employed.

In a preferred embodiment of the invention, a MPO composition includes at least two species of MPOs wherein the species having the highest melting temperature is present in an amount less than or equal to 10%, preferably less than or equal to 5%, more preferably less than or equal to 3%.

In one embodiment, the MPOs in the MPO composition have a DP from 2 to about 20. In another embodiment, the MPOs have a DP from 2 to about 10. In another embodiment, the MPOs have a DP from 2 to about 8. In yet another embodiment, the MPOs have a DP from 2 to about 6.

In one embodiment, the species having the highest melting temperature is macrocyclic polyester tetramer. In one embodiment, the MPO composition includes macrocyclic PBT oligomers. In another embodiment, the MPO composition includes macrocyclic PET oligomers. The MPO composition may contain homo-oligomer, co-oligomer, or both. In one embodiment, the MPO composition includes a macrocyclic co-polyester oligomer that has at least about 90% mole percent PBT structural units.

In one embodiment, the MPO composition includes 30-40% macrocyclic polyester dimers, 30-45% macrocyclic polyester trimers, 0-5% macrocyclic polyester tetramers, and 5-20% macrocyclic polyester pentamers. In some embodiments, the percentage of macrocyclic polyester tetramers preferably is less than about 3%, more preferably less than about 2%, or most preferably less than about 1%.

In one embodiment, the MPO composition includes a filler. In another embodiment, the MPO composition includes a polymerization catalyst. In another embodiment, the MPO composition is part of a prepreg composition.

MPO compositions in which a major proportion of the macrocyclic polyester tetramer has been removed have melting temperatures significantly lower than those of corresponding compositions containing macrocyclic polyester tetramer in the original proportions, i.e., the unmodified product mixtures (equilibrated or nearly equilibrated) of the MPO-forming reactions. The melting temperatures typically are wide ranges by reason of the various kinds of MPO molecules in the MPO compositions. The most pronounced decrease in temperature is in the upper value of the range, i.e., the temperature at which the last trace of solid melts. Typically, the upper value of the melting temperature range of a modified MPO composition may be from about 15°C to as much as 70°C lower than the upper value for the unmodified original MPO composition.

This decrease in melting temperature is typically accompanied by a significant decrease in crystallinity, particularly upon heating above the melting temperature followed by quenching. Thus, MPO compositions in which macrocyclic polyester tetramer has been removed can be quenched and used to impregnate fibrous or other fillers, whereupon a prepreg composition capable of being draped and shaped is produced.

III. Polymerization catalysts

Polymerization catalysts that may be employed in the invention are capable of catalyzing the polymerization of MPOs. Organotin and organotitanate compounds are preferred catalysts, although other catalysts may be used. For example, organotin compound 1,1,6,6-tetra-n-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane may be used as polymerization catalyst. Other illustrative organotin compounds include n-butyltin(IV) chloride dihydroxide, dialkyltin(IV) oxides, such as di-n-butyltin(IV) oxide and di-n-octyltin oxide, and acyclic and cyclic monoalkyltin(IV) derivatives such as n-butyltin tri-n-butoxide, dialkyltin(IV) dialkoxides such as di-n-butyltin(IV) di-n-butoxide and 2,2-di-n-butyl-2-stanna-1,3-dioxacycloheptane, and

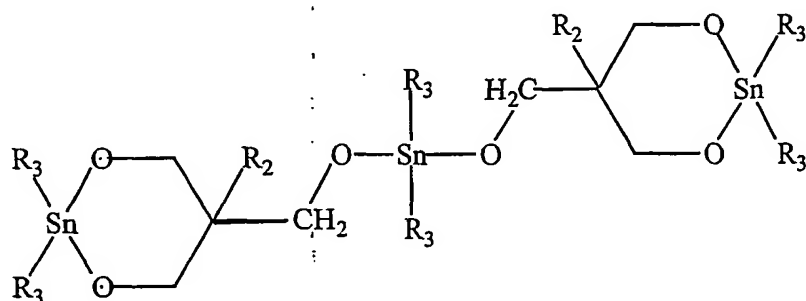
- 11 -

trialkyltin alkoxides such as tributyltin ethoxide. *See, e.g., U.S. Patent No. 5,348,985 to Pearce et al.*

Also, trisstannoxanes having the general formula (I) shown below can be used as a polymerization catalyst to produce branched polyester polymers.

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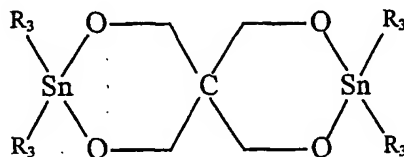
(I)



where R_2 is a C_{1-4} primary alkyl group and R_3 is C_{1-10} alkyl group.

10 Additionally, organotin compounds with the general formula (II) shown below can be used as a polymerization catalyst to prepare branched polyester polymers from MPOs.

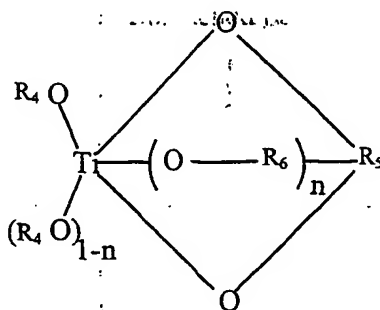
(II)



15 where R_3 is defined as above.

As for titanate compounds, tetra(2-ethylhexyl) titanate, tetraisopropyl titanate, tetrabutyl titanate, and titanate compounds with the general formula (III) shown below can be used as polymerization catalysts.

(III)



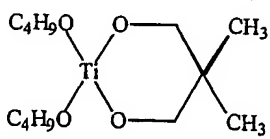
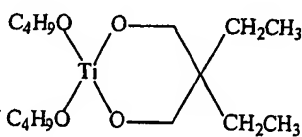
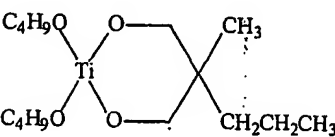
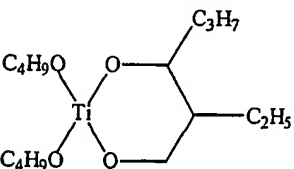
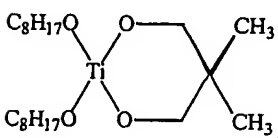
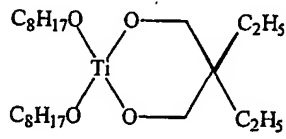
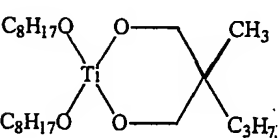
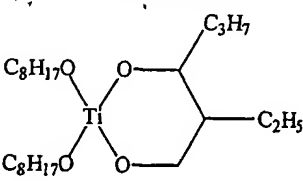
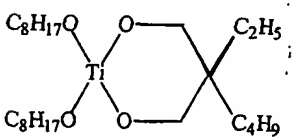
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wherein: each R_4 is independently an alkyl group, or the two R_4 groups taken together form a divalent aliphatic hydrocarbon group; R_5 is a C_{2-10} divalent or trivalent aliphatic hydrocarbon group; R_6 is a methylene or ethylene group; and n is 0 or 1.

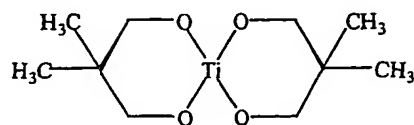
Typical examples of titanate compounds with the above general formula are shown in

5 Table 1.

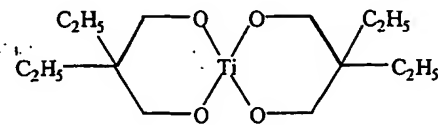
Table 1. Examples of Titanate Compounds Having Formula (III)

 <p>Di-1-butyl 2,2-dimethylpropane-1,3-dioxytitanate</p>	 <p>Di-1-butyl 2,2-diethylpropane-1,3-dioxytitanate</p>
 <p>Di-1-butyl 2-(1-propyl)-2-methylpropane-1,3-dioxytitanate</p>	 <p>Di-1-butyl 2-ethylhexane-1,3-dioxytitanate</p>
 <p>Di(2-ethyl-1-hexyl) 2,2-dimethylpropane-1,3-dioxytitanate</p>	 <p>Di(2-ethyl-1-hexyl) 2,2-diethylpropane-1,3-dioxytitanate</p>
 <p>Di(2-ethyl-1-hexyl) 2-(1-propyl)-2-methylpropane-1,3-dioxytitanate</p>	 <p>Di(2-ethyl-1-hexyl) 2-ethylhexane-1,3-dioxytitanate</p>
 <p>Di(2-ethyl-1-hexyl) 2-(1-butyl)-2-ethylpropane-1,3-dioxytitanate</p>	

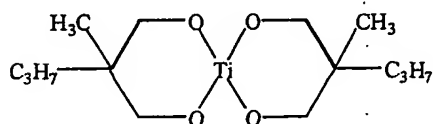
- 13 -

Table 1. Examples of Titanate Compounds Having Formula (III) (Cont'd)

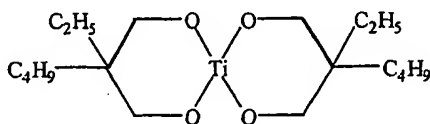
Bis(2,2-dimethyl-1,3-propylene) titanate



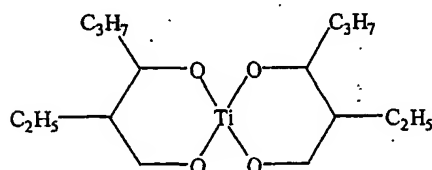
Bis(2,2-diethyl-1,3-propylene) titanate



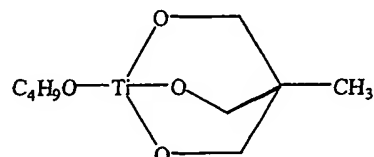
Bis(2-(1-propyl)-2-methyl-1,3-propylene) titanate



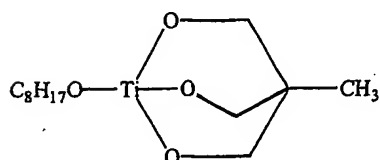
Bis(2-(1-butyl)-2-ethyl-1,3-propylene) titanate



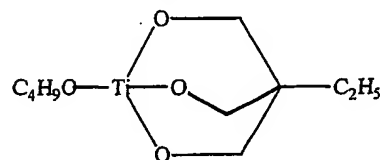
Bis(2-ethyl-1,3-hexylene) titanate



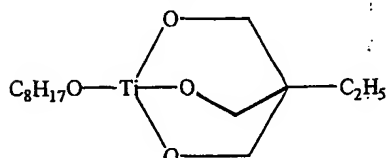
1-(1-Butoxy)-4-methyl-2,6,7-trioxabicyclo[2,2,2]octane



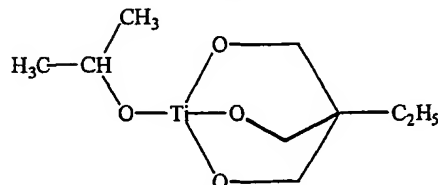
1-(2-ethyl-1-hexoxy)-4-methyl-2,6,7-trioxabicyclo[2,2,2]octane



1-(1-Butoxy)-4-ethyl-2,6,7-trioxabicyclo[2,2,2]octane



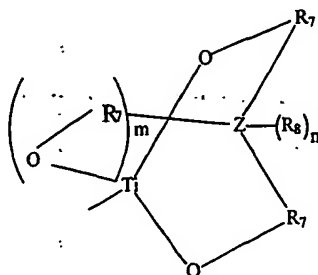
1-(2-ethyl-1-hexoxy)-4-ethyl-2,6,7-trioxabicyclo[2,2,2]octane



1-(2-Propoxy)-4-ethyl-2,6,7-trioxabicyclo[2,2,2]octane

- 5 Titanate ester compounds having at least one moiety of the following general formula have also been used as polymerization catalysts:

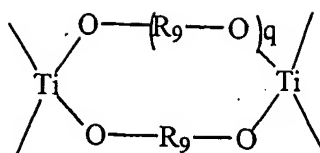
(IV)



or

- 14 -

(V)



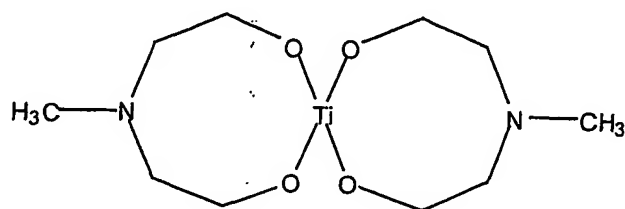
wherein:

each R_7 is independently a C_{2-3} alkylene group;5 R_8 is a C_{1-6} alkyl group or unsubstituted or substituted phenyl group;Z is O or N; provided when Z is O, $m = n = 0$, and when Z is N, $m = 0$ or 1 and $m + n = 1$;each R_9 is independently a C_{2-6} alkylene group; and q is 0 or 1.

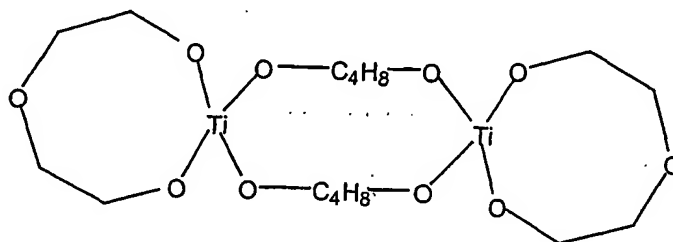
Typical examples of such titanate compounds are shown below as formula (VI) and formula (VII):

10

(VI)



(VII)



IV. The Blend Material

15 A blend material comprising MPOs and a polymerization catalyst allows for easy production, storage, transportation and processing. From the standpoint of applications, the blend material is a one-component ready-to-use mixture. The blend material may also be processed like a thermoset while producing a thermoplastic. Furthermore, the blend material may eliminate the need for existing equipment to be modified to allow for transfer of the MPO and a polymerization catalyst into the equipment in the appropriate amounts at the appropriate

20 time and at the appropriate temperature.

- 15 -

In one aspect, the invention relates to a blend material comprising a MPO composition with a modified physical property (e.g., the melting temperature as described above) and a polymerization catalyst.

There is no limitation with respect to the physical form of the MPO when mixed with the polymerization catalyst as long as the MPO remains substantially chemically intact. In one embodiment, the MPO is a solid such as a powder. In this embodiment, mechanical mixing typically is used to mix MPO with a polymerization catalyst. In another embodiment, the MPO is mixed in the presence of a solvent with the solvent remaining present during the step of mixing.

In one embodiment, the blend material also includes a filler as described above. Illustrative examples of such fillers include pigments, light weight fillers, flame retardants, and ultraviolet light stabilizers. For example, calcium carbonate may be used to increase the thickness of a polyester polymer product to improve its mechanical performance. Also, glass microspheres may be added to lower the density of the product. Other fillers include nanoclays, e.g., to increase the modulus of the product, organobromides in combination with antimony oxides, e.g., to impart flame resistance, and colorants such as carbon black or titanium dioxide.

The filler is added generally between about 0.1% and 70% by weight, between about 25% and 70% by weight, or between about 2% and 5% by weight depending on the filler and the purpose for adding the filler. For example, the percentage is preferably between 25% and 50% by weight in the case of calcium carbonate, between 2% and 5% by weight in the case of nanoclays, between 0.1% and 1% in the case of pigments, and between 25% and 70% by weight in the case of glass microspheres.

A process for preparing the blend material includes providing a MPO and mixing the MPO with a polymerization catalyst. When preparing the blend, the MPO and the polymerization catalyst may be mixed together by various means. For example, any conventional mixer or blender may be employed to mix the MPO with the polymerization catalyst via agitation at temperatures below the melting temperature of the MPO. This process may be conducted under an inert atmosphere such as a nitrogen atmosphere.

A solvent may also be employed to assist in the uniform mixing of the MPO with the polymerization catalyst. Various solvents can be used, and there is no limitation with respect to the type of solvent that may be used other than that the solvent is substantially free of water. Illustrative examples of solvents that may be employed in the invention include methanol,

- 16 -

ethanol, isopropanol, acetone, methyl ethyl ketone, benzene, toluene, *o*-xylene, chlorobenzene, dichloromethane, and chloroform.

There is no limitation with respect to the amount of solvent to be employed other than that the amount results in a uniform mixing of the MPO and the polymerization catalyst. In one
5 embodiment, the blend of MPO with the polymerization catalyst is isolated either by direct removal of the solvent via evaporation or by precipitation via addition of the mixture into a nonsolvent. In another embodiment, the blend of solid ingredients is further dried under vacuum at elevated temperatures below the melting temperature of the MPO to remove any residual solvent.

10 A process for preparing the blend material further having at least one filler, or any other additional material, is generally the same as described above, however, the characteristics of the filler and/or additional materials must be considered. It should be understood that the MPO, the polymerization catalyst, the filler, any additional material(s) and/or solvent, if used, may be mixed in any order or simultaneously as long as the final composition contains the appropriate
15 amount of each ingredient.

It is within the scope of the invention to employ one, two or more different fillers in preparing a blend material of MPO and polymerization catalyst. Unless specifically stated otherwise, any embodiment of a composition, article or process that refers to filler in singular also includes an embodiment wherein two or more different fillers are employed. Similarly,
20 unless stated otherwise, any embodiment of a composition, article or process that refers to fillers in plural also includes an embodiment wherein one filler is employed.

In one embodiment of the invention, the amount of polymerization catalyst employed is generally about 0.01 to about 10.0 mole percent, preferably about 0.1 to about 2 mole percent, and more preferably about 0.2 to about 0.6 mole percent based on total moles of monomer repeat
25 units of the MPO.

Although dependent on the particular composition of the blend material, blend materials typically exhibit a shelf life generally longer than a week, and preferably longer than a month, and more preferably longer than a year when stored at ambient temperature.

It is within the scope of the invention to employ one, two or more different
30 polymerization catalysts in preparing a blend of MPO and polymerization catalyst. Unless specifically stated otherwise, any embodiment of a composition, article or process that refers to polymerization catalyst in singular also includes an embodiment wherein two or more different polymerization catalysts are employed. Similarly, unless stated otherwise, any embodiment of a

- 17 -

composition, article or process that refers to polymerization catalyst in plural also includes an embodiment wherein one polymerization catalyst is employed. Two or more polymerization catalysts may be used to vary the rate of polymerization and to produce polyesters with variable degrees of branching.

5 **V. Polymerization of MPOs**

 In another aspect, the invention relates to a process for polymerizing a MPO composition that includes the steps of (a) providing a MPO composition with a modified physical property (e.g., the melting temperature as described above), (b) providing a polymerization catalyst, and (c) polymerizing the MPOs. The MPOs and the polymerization catalyst may be components of a
10 blend material. Therefore, in one embodiment, a process for polymerizing a MPO composition includes the steps of (a) providing a blend material having a MPO composition with a modified physical property, e.g., the melting temperature, and (b) polymerizing the MPOs. In one embodiment, the polymerization is conducted in the range of 130 °C to 230 °C.

 By reason of the lower melting temperature and decrease in crystallinity, it is frequently
15 possible to polymerize the compositions of the present invention to linear polyesters at lower temperatures than with previously known MPO compositions. For example, a conventionally prepared macrocyclic PBT oligomer composition may require a polymerization temperature (in the presence of a conventional tin compound as catalyst) on the order of 190°C and will not polymerize at 150°C. The corresponding composition, from which most of the tetramer has been
20 removed according to this invention, has been polymerized to high molecular weight PBT at temperatures as low as 148°C.

 In other respects, the compositions of MPOs in which tetramers have been removed are similar to known MPO compositions in that they may be polymerized under a wide variety of conditions in the presence of polymerization catalysts to linear polyesters having a wide variety
25 of uses.

 Blends of MPOs with catalyst and/or filler may be polymerized in processes such as rotational molding, resin film infusion, pultrusion, resin transfer molding, filament winding, making and using powder-coated or hot melt prepreg, water slurry process, compression molding, and roll wrapping. These processes may be used to form polyester compositions,
30 including composites, which may be included in articles of manufacture such as carbon fiber golf shafts and lightweight automotive chassis members, construction materials, and so on.

- 18 -

The following examples are provided to further illustrate and to facilitate the understanding of the invention. These specific examples are intended to be illustrative of the invention.

Example A General Depolymerization Procedure

5 Dissolve dry poly(1,4-butylene terephthalate) (PBT) pellets in dry *o*-dichlorobenzene (ODCB) under inert atmosphere at 180°C. Add a titanate catalyst as a solution in ODCB or as a neat solid. The depolymerization reaction is carried out at about 180°C. The reaction can be sampled over time to determine progress. When equilibrium is reached (usually within 1 hour), the reaction is cooled to 100°C and water is added to quench the titanate catalyst
10 (add about 0.5% water by volume). After quenching, the reaction mixture is concentrated by removing 70-95% of the ODCB. This step can be done from 70-180°C by adjusting pressure during the strip.

After the initial concentration step, the reaction is allowed to cool to about 70°C and filtered to remove the bulk of the linears which fall from solution. The filtrate, which contains
15 the MPOs, is concentrated to about 30% solids at about 110°C. An equal volume of heptane is added and the reaction is allowed to cool to about 70°C to precipitate the PBT tetramer. Filter to remove the PBT tetramer and pass the filtrate through a column of alumina to remove residual linears. Pure MPOs are then isolated by heptane precipitation or by concentration.

PBT used in these experiments was produced by General Electric (Valox 315 grade) and
20 was dried in *vacuo* at about 120°C before use. Anhydrous ODCB was used as received from Aldrich. Titanate catalysts were prepared from tetraisopropyl titanate from DuPont that was vacuum distilled prior to use. Diols that were dried over molecular sieves. All other reagent grade solvents and chemicals were used as received.

HPLC analysis was used to characterize the composition of the MPOs and to follow
25 progression of depolymerization reactions. HPLC analysis was conducted using a Hewlett Packard Series 1050 chromatography system. Samples were eluted at 1.5 ml/min through a 4.6 x 15 cm Zorbax Eclipse XBD-C8 column at 40°C. A linear acetonitrile:water gradient which ramped from 50:05 to 100:0 over 18 min was used. Analysis was calibrated using pure PBT
30 dimer which was isolated by vacuum sublimation. MPOs were quantified using phenanthrene as an internal calibration standard. Peaks were measured at 254 nm with a UV detector.

Analyses for polymer M_w were conducted using a Hewlett Packard Series 1100 chromatography system. Samples were eluted at 1 ml/min with chloroform through a bank of

- 19 -

two Phenomenex Phenogel 5 μ m linear 300 x 7.8 mm columns at 40°C. Peaks were detected with a UV detector at 254 nm and the instrument was calibrated using polystyrene standards.

HPLC retention times of MPOs are shown in Table 1. Melting range data of select MPO compositions is shown in Table 2.

5

Table 1. HPLC Retention Times of Select MPOs

MPO	Dimer (PBT)	Trimer (PBT)	Tetramer (PBT)	Pentamer (PBT)
HPLC T _r (min.)	6.8	11.5	13.6	15.4

Table 2. Melting Ranges of Select MPO Compositions

Sample	%Dimer	%Trimer	%Tetramer	%Pentamer	% co-MPO	Melt Range °C
a	13.1	12.9	51.9	11.7	9.3	175-218
b	2	46.7	29.8	21.5	0	120-215
c	32.2	38.2	16.6	13.1	0	120-200
d	34.5	29.9	12.8	11.2	13.8	125-175
e	30.6	34.3	10.2	10.2	14.2	125-168
f	37.1	37	1.48	10	14.5	125-148

10 *Example 1*

A 22.2 g sample of commercially available PBT was dissolved in 1,450 g (1,107 ml) of ODCB and depolymerized in the presence of 2.8 mole percent of a mixed 1,4-butanediol/2-methyl-2,4-pentanediol (4.3:1 molar) titanate catalyst. MPOs were obtained in the amount of 11.4 g, or 51.8% of theoretical.

15 The reaction mixture was quenched with water at 100°C and ODCB was distilled off to a MPO concentration of 11% by weight (71 ml of ODCB). A sample was removed and stripped of solvent; it was found to have a melting temperature of 100-210°C.

Heptane, 71 ml, was added to the remaining oligomer composition at 110°C and the reaction mixture was allowed to cool to 70°C, whereupon a precipitate formed. The mixture was
 20 filtered; the filtration residue was found by HPLC analysis to contain about 96% by weight of the tetramer in the reaction product. The filtrate was poured into an excess of heptane to precipitate the remaining oligomers which were found to have a melting temperature of 100-150°C.

Example 2

A 250 ml round-bottomed flask equipped with a magnetic stirrer was charged with 85 g
 25 (64 ml) of ODCB and 15 g of a macrocyclic PBT oligomer composition prepared by the reaction

- 20 -

of terephthaloyl chloride with bis(4-hydroxybutyl) terephthalate. A control sample of the oligomer composition was found to have a melting temperature of 100-180°C.

Heptane, 64 ml, was added slowly to the remaining oligomer composition at 110°C and the reaction mixture was allowed to cool over 1 hour to 75°C, whereupon a precipitate formed.

5 The mixture was filtered; the filtration residue was found to contain about 90% by weight of the cyclic tetramer in the reaction product. The filtrate was poured into an excess of heptane to precipitate the remaining oligomers which were found to have a melting temperature of 100-130°C.

Example 3

10 A 3 l round-bottomed flask equipped with a magnetic stirrer and thermometer was charged with 700 g (534 ml) of ODCB and 300 g of a macrocyclic PBT oligomer composition prepared by the reaction of terephthaloyl chloride with 1,4-butanediol. A control sample of the oligomer composition was found to have a melting temperature of 120-175°C.

15 The mixture was heated to 110°C to dissolve all of the oligomers and heptane, 534 ml, was added slowly at 110°C. The reaction mixture was allowed to cool to 75°C, whereupon a precipitate formed. The mixture was filtered; the filtration residue was found to contain about 73% by weight of the cyclic tetramer in the reaction product. The filtrate was poured into an excess of heptane to precipitate the remaining oligomers which were found to have a melting temperature of 120-158°C.

20 Example 4

A 5% (by weight) solution in ODCB of macrocyclic PBT oligomers, prepared as described in Example 1, was found to be a homogeneous liquid at 110°C. Upon cooling to room temperature, a precipitate deposited from the solution. The precipitate was found by analysis to be 90% pure cyclic tetramer, and to constitute 60% by weight of the tetramer present in the
25 original oligomer composition.

Example 5

A 300 mg control sample of the PBT oligomer composition employed in Example 2, from which the tetramer had not been removed, was placed in a test tube and submerged in an oil bath maintained at 150°C for 10 minutes. The composition did not melt at this temperature. A
30 sample of the product of Example 2, from which tetramer had been removed, melted when heated to the same temperature but crystallized to an opaque, brittle solid upon cooling.

- 21 -

When the product of Example 2 was heated to 150°C and quenched by submersion in cold water, it remained transparent, indicating that it was amorphous rather than crystalline after quenching. It remained amorphous and tacky after storing at ambient temperature for one month. By contrast, the control returned to a brittle, crystalline state upon standing for 48 hours.

5 **Example 6**

A 3 l round-bottomed flask was charged with 3,098 ml of ODCB, 26.3 g of commercially available PBT pellets, and 4.9 g of tetramer removed from a MPO composition as described in Example 3. The resulting mixture was heated to 180°C until all solids were dissolved and a titanate catalyst similar to that of Example 1 was added in a similar proportion to PBT. Heating
10 at 180°C was continued for one hour, after which a portion of the mixture was analyzed and found to contain MPOs in a proportion similar to that observed in Example 1.

While typical embodiments have been set forth for the purpose of illustration, the foregoing descriptions and examples should not be deemed to be a limitation on the scope of the invention. Accordingly, various modifications, adaptations, and alternatives may occur to one
15 skilled in the art without departing from the spirit and scope of the present invention.

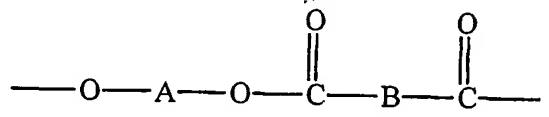
The patents and references referred to above are incorporated by reference including:
U.S. Patent Nos. 5,039,783, 5,191,013, 5,231,161, 5,348,985, 5,389,719, 5,407,984, 5,466,744,
5,591,800, 5,661,214, 5,668,186, and 5,710,086.

What is claimed is:

- 22 -

- 1 1. A process for modifying a physical property of a composition comprising macrocyclic
2 polyester oligomers, comprising the steps of:

3 (a) providing a composition comprising at least two species of macrocyclic
4 polyester oligomers, each of said macrocyclic polyester oligomers comprising a structural
5 repeat unit of the formula



7 wherein

8 A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group, and
9 B is a divalent aromatic or alicyclic group; and

10 (b) changing the weight percentage of at least one species of said macrocyclic
11 polyester oligomers in said composition.

- 1 2. The process of claim 1 wherein said physical property is the melting temperature of said
2 composition.

- 1 3. The process of claim 1 wherein said at least one species of said macrocyclic polyester
2 oligomers in step (b) is the highest melting temperature macrocyclic polyester oligomer in
3 said composition.

- 1 4. The process of claim 1 wherein said at least one species of said macrocyclic polyester
2 oligomers in step (b) comprises at least said macrocyclic polyester tetramer.

- 1 5. The process of claim 4 wherein step (b) comprises reducing the weight percentage of at
2 least the macrocyclic polyester tetramer.

- 1 6. The process of claim 1 wherein said at least two species of macrocyclic polyester
2 oligomers in step (a) have a degree of polymerization from 2 to 10.

- 1 7. The process of claim 6 wherein said at least two species of macrocyclic polyester
2 oligomers in step (a) have a degree of polymerization from 2 to 6.

- 1 8. The process of claim 1 wherein said composition comprises macrocyclic poly(1,4-
2 butylene terephthalate) oligomers.

- 23 -

1 9. The process of claim 1 wherein said composition comprises macrocyclic poly(ethylene
2 terephthalate) oligomers

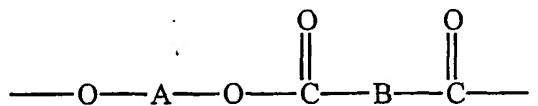
1 10. The process of claim 1 wherein said composition comprises a macrocyclic copolyester
2 oligomer

1 11. The process of claim 10 wherein said composition comprises a macrocyclic copolyester
2 oligomer containing at least about 90 mole percent poly(1,4-butylene terephthalate)
3 structural units.

1 12. The process of claim 1 wherein step (b) comprises performing fractional crystallization.

1 13. A macrocyclic polyester oligomer composition having a decreased melting temperature
2 produced by the process of claim 1.

1 14. A macrocyclic polyester oligomer composition comprising at least two species of
2 macrocyclic polyester oligomers, each of said macrocyclic polyester oligomers
3 comprising a structural repeat unit of the formula



4
5 wherein

6 A is an alkylene, a cycloalkylene or a mono- or polyoxyalkylene group, and

7 B is a divalent aromatic or alicyclic group,

8 wherein a species of said macrocyclic polyester oligomers having the highest melting
9 temperature is present in an amount less than or equal to 5%.

1 15. The composition of claim 14 wherein each of said macrocyclic polyester oligomers has a
2 degree of polymerization in the range from 2 to about 6.

1 16. The composition of claim 15 wherein said species having the highest melting temperature
2 is macrocyclic polyester tetramer.

1 17. The composition of claim 14 wherein said macrocyclic polyester oligomers comprise
2 macrocyclic poly(1,4-butylene terephthalate) oligomers.

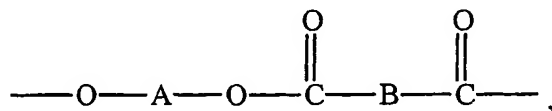
- 24 -

- 1 18. The composition of claim 14 wherein said macrocyclic polyester oligomers comprise
2 macrocyclic poly(ethylene terephthalate) oligomers.
- 1 19. The composition of claim 15 wherein said macrocyclic polyester oligomers comprise a
2 macrocyclic copolyester oligomer comprising at least about 90 mole percent poly(1,4-
3 butylene terephthalate) structural units.
- 1 20. The composition of claim 14 further comprising a filler.
- 1 21. The composition of claim 14 further comprising a polymerization catalyst.
- 1 22. A prepreg composition comprising the composition of claim 14.
- 1 23. A blend material comprising:
2 (a) the macrocyclic polyester oligomer composition of claim 14; and
3 (b) a polymerization catalyst.
- 1 24. The blend material of claim 23 further comprising a filler.
- 1 25. The blend material of claim 24 wherein said filler is present at a weight
2 percentage of from 0.1% to 70%.
- 1 26. A polyester polymer composite prepared by polymerizing said macrocyclic
2 polyester oligomers of said blend material of claim 23.
- 1 27. An article of manufacture comprising said polyester polymer composite of claim
2 26.
- 1 28. A process for polymerizing a macrocyclic polyester oligomer composition
2 comprising the steps of:
3 (a) providing the macrocyclic polyester oligomer composition of claim 14;
4 (b) providing a polymerization catalyst; and
5 (c) polymerizing said macrocyclic polyester oligomers.
- 1 29. A process for polymerizing a macrocyclic polyester oligomer composition
2 comprising the steps of:
3 (a) providing the blend material of claim 23; and
4 (b) polymerizing said macrocyclic polyester oligomers.

- 25 -

1 30. The process of claim 29 wherein step (b) is conducted at a temperature between
2 130°C and 230°C.

1 31. A macrocyclic polyester oligomer composition comprising 30-40% macrocyclic polyester
2 dimers, 30-45% macrocyclic polyester trimers, 0-5% macrocyclic polyester tetramers, and
3 5-20% macrocyclic polyester pentamers, each of said macrocyclic polyester oligomers
4 comprising a structural repeat unit of the formula

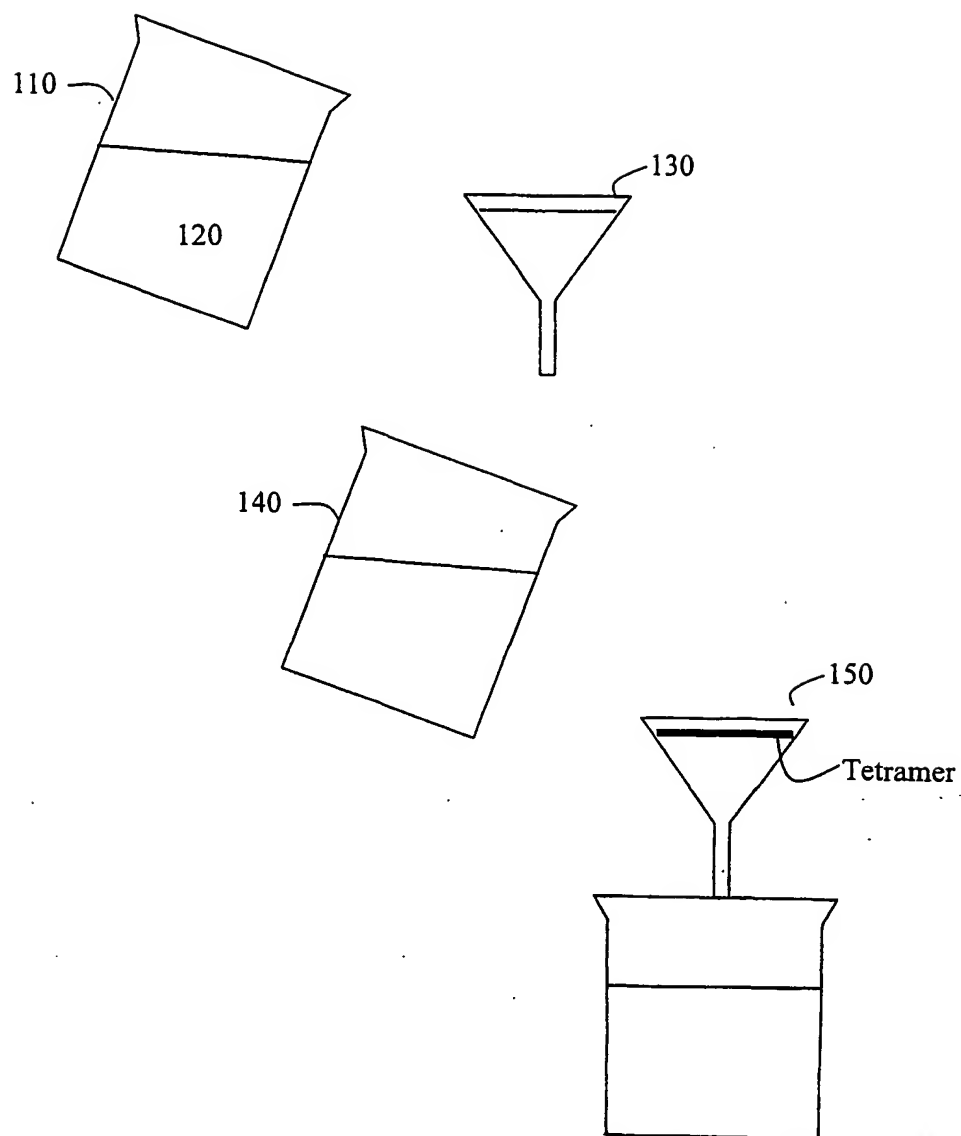


6 wherein

7 A is an alkylene, a cycloalkylene or a mono- or polyoxyalkylene group, and

8 B is a divalent aromatic or alicyclic group.

1 32. The composition of claim 31 wherein said macrocyclic polyester oligomer composition
2 comprises less than 3% of macrocyclic polyester tetramers.

**Fig. 1**

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(54) Title: SPECIES MODIFICATION IN MACROCYCLIC POLYESTER OLIGOMERS, AND COMPOSITIONS PREPARED THEREBY

(57) Abstract: Physical properties, such as melting temperature of MPO compositions may be significantly modified by modifying the weight percentage of one or more of the constituent MPOs. For example, removal of a significant portion of the tetramer can afford low melting MPO compositions. In one aspect, the invention is related to a method for modifying a physical property of a MPO composition that includes the steps of (a) providing a composition that has at least two species of MPOs, and (b) changing the weight percentage of at least one species of the MPOs in the composition. In another aspect, the invention is related to a MPO composition that includes at least two species of MPOs where a species of the MPOs having the highest melting temperature is present in an amount less than or equal to 5 %. In yet another aspect, the invention is related to a MPO composition comprising 30-40 % macrocyclic polyester dimers, 30-45 % macrocyclic polyester trimers, 0-5 % macrocyclic polyester tetramers, and 5-20 % macrocyclic polyester pentamers.

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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 601 753 A (GEN ELECTRIC) 15 June 1994 (1994-06-15)	1-11, 13-32
Y	claims 1-13	12
Y	GB 1 108 921 A (DU PONT) 10 April 1968 (1968-04-10) page 5, line 1 - line 12	12
X	US 5 191 013 A (COOK TODD D ET AL) 2 March 1993 (1993-03-02) cited in the application claims 1,2; example 26	1-32

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

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O document referring to an oral disclosure, use, exhibition or other means

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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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(54) Title: SPECIES MODIFICATION IN MACROCYCLIC POLYESTER OLIGOMERS, AND COMPOSITIONS PREPARED THEREBY

(57) Abstract: Physical properties, such as melting temperature of MPO compositions may be significantly modified by modifying the weight percentage of one or more of the constituent MPOs. For example, removal of a significant portion of the tetramer can afford low melting MPO compositions. In one aspect, the invention is related to a method for modifying a physical property of a MPO composition that includes the steps of (a) providing a composition that has at least two species of MPOs, and (b) changing the weight percentage of at least one species of the MPOs in the composition. In another aspect, the invention is related to a MPO composition that includes at least two species of MPOs where a species of the MPOs having the highest melting temperature is present in an amount less than or equal to 5 %. In yet another aspect, the invention is related to a MPO composition comprising 30-40 % macrocyclic polyester dimers, 30-45 % macrocyclic polyester trimers, 0-5 % macrocyclic polyester tetramers, and 5-20 % macrocyclic polyester pentamers.

SPECIES MODIFICATION IN MACROCYCLIC POLYESTER OLIGOMERS, AND
COMPOSITIONS PREPARED THEREBYTechnical Field

This invention generally relates to thermoplastics and articles formed therefrom. More particularly, the invention relates to macrocyclic polyester oligomer compositions and methods for modifying physical and chemical properties of the compositions. Even more particularly, this invention relates to macrocyclic polyester oligomer compositions having relatively low melting
5 temperatures.

Background Information

Linear polyesters such as poly(alkylene terephthalate) are generally known and commercially available where the alkylene typically has 2 to 8 carbon atoms. Linear polyesters have many valuable characteristics including strength, toughness, high gloss and solvent
10 resistance. Linear polyesters are conventionally prepared by the reaction of a diol with a dicarboxylic acid or its functional derivative, typically a diacid halide or ester. Linear polyesters may be fabricated into articles of manufacture by a number of known techniques including extrusion, compression molding, and injection molding. Linear polyesters may be produced from macrocyclic polyester oligomers.

15 Macrocyclic polyester oligomers (MPOs) have unique properties that make them attractive as matrices for engineering thermoplastic composites. These desirable properties stem from the fact that MPOs exhibit low melt viscosity, allowing them to impregnate a dense fibrous preform easily. Furthermore, certain MPOs melt and polymerize at temperatures well below the melting point of the resulting polymer. Upon melting and in the presence of an appropriate
20 catalyst, polymerization and crystallization can occur virtually isothermally. As a result, the time and expense required to thermally cycle a tool is favorably reduced.

Generally speaking, MPO compositions have high melting temperatures, which necessitate the use of special equipment in processing not commonly available in polymer processing units. If compositions with lower melting temperatures could be produced, it would
25 be possible to use more readily available processing equipment such as that is commonly used in the production and handling of epoxy resins.

Summary of the Invention

Physical and/or chemical properties of MPO compositions may be significantly modified by modifying the weight percentage of one or more of the constituent MPOs. For example, the presence of a single MPO species, the macrocyclic polyester tetramer, has an unexpectedly pronounced effect on the melting temperature of a MPO composition. Removal of a portion of the macrocyclic polyester tetramer can result in low-melting MPO compositions. The resulting MPO compositions have the further advantage, under many circumstances, of a greatly reduced tendency to crystallize at ambient temperatures, making it possible to combine them with fillers such as carbon or glass fibers to produce prepregs easily convertible to filled high molecular weight linear polyesters.

In one aspect, the invention is related to a process for modifying a physical property of a composition that includes MPOs. The process includes the steps of (a) providing a composition that has at least two species of MPOs, and (b) changing the weight percentage of at least one species of the MPOs in the composition.

In another aspect, the invention is related to a MPO composition that includes at least two species of MPOs wherein a species of the MPOs having the highest melting temperature is present in an amount less than or equal to 5%. In one embodiment, a blend material includes such a MPO composition and also a polymerization catalyst.

In a preferred embodiment, a MPO composition of the invention comprises 30-40% macrocyclic polyester dimers, 30-45% macrocyclic polyester trimers, 0-5% macrocyclic polyester tetramers, and 5-20% macrocyclic polyester pentamers.

The foregoing and other objects, aspects, features, and advantages of the invention will become more apparent from the following figures, description, and claims.

Brief Description of Figures

The drawings are not necessarily to scale, emphasis instead being generally placed upon illustrating the principles of the invention to facilitate its understanding.

FIG. 1 is a schematic illustration of an embodiment of the invention including a fractional crystallization process.

Detailed Description

Physical properties, for example, the melting temperatures, of a composition comprising MPOs may be modified by modifying the weight percentage of a MPO species, for example, the macrocyclic polyester tetramer. A MPO composition having a low melting temperature can be

polymerized and processed at lower temperature thereby avoiding the need for special equipment not commonly available in polymer processing.

Definitions

5 The following general definitions may be helpful in understanding the various terms and expressions used in this specification.

As used herein, "macrocyclic" means a cyclic molecule having at least one ring within its molecular structure that contains 8 or more atoms covalently connected to form the ring.

As used herein, an "oligomer" means a molecule that contains 2 or more identifiable structural repeat units of the same or different formula.

10 As used herein, a "macrocyclic polyester oligomer (MPO)" means a macrocyclic oligomer containing structural repeat units having an ester functionality. A MPO typically refers to multiple molecules of one specific formula. However, a MPO also may include multiple molecules of different formulae having varying numbers of the same or different structural repeat units. In addition, a MPO may be a macrocyclic co-polyester oligomer (including macrocyclic
15 multi-polyester oligomer), i.e., an oligomer having two or more different structural repeat units having an ester functionality within one cyclic molecule.

As used herein, "degree of polymerization (DP)" means the number of identifiable structural repeat units in oligomeric or polymeric backbone. The structural repeat units may have the same or different molecular structural. For example, "macrocyclic polyester tetramer" or
20 "tetramer" refers to MPOs with a DP of 4.

As used herein, a "species" means MPOs having the same DP. For example, the macrocyclic polyester tetramer is one species.

As used herein, a "macrocyclic polyester oligomer composition" means a composition comprising a mixture of MPOs having different DP values, whether or not units of more than one
25 molecular structure are present.

As used herein, a "blend material" means a mixture of two or more components including at least one MPO and at least one polymerization catalyst. Preferably the blend material is uniformly mixed. A blend material may also include a filler as well as other components recognized by a skilled artisan.

30 As used herein, "substantially homo- or co-polyester oligomer" means a polyester oligomer wherein the structural repeat units are substantially identical or substantially two different structural repeat units, respectively.

As used herein, "an alkylene group" means $-C_nH_{2n}-$, where $n \geq 2$.

As used herein, "a cycloalkylene group" means a cyclic alkylene group, $-C_nH_{2n-x}-$, where x represents the number of H's replaced by cyclization(s).

As used herein, "a mono- or polyoxyalkylene group" means $[-(CH_2)_m-O-]_n-(CH_2)_m-$, wherein m is an integer greater than 1 and n is an integer greater than 0.

5 As used herein, "a divalent aromatic group" means an aromatic group with links to other parts of the macrocyclic molecule. For example, a divalent aromatic group may include a meta- or para- linked monocyclic aromatic group (e.g., benzene).

As used herein, "an alicyclic group" means a non-aromatic hydrocarbon group containing a cyclic structure within.

10 As used herein, "a filler" means a material other than a MPO or a polymerization catalyst that may be included in the blend material. A filler often is included to achieve a desired purpose or property, and may be present in the resulting polyester polymer. For example, the purpose of the filler may be to provide stability, such as chemical, thermal or light stability, to the blend material or the polyester polymer product, and/or to increase the strength of the polyester
15 polymer product. A filler also may provide or reduce color, provide weight or bulk to achieve a particular density, provide flame resistance (i.e., be a flame retardant), be a substitute for a more expensive material, facilitate processing, and/or provide other desirable properties as recognized by a skilled artisan. Illustrative examples of fillers are, among others, fumed silica, carbon black, titanium dioxide, organo bromides in combination with antimonium oxides, calcium carbonate,
20 chopped fibers, fly ash, glass microspheres, micro-balloons, crushed stone, nanoclay, linear polymers, and monomers.

As used herein, "a polyester polymer composite" means a polyester polymer that is associated with another substrate such as, a fibrous or particulate material. Illustrative examples of particulate materials are chopped fibers, glass microspheres, and crushed stone.

25 As used herein, "an equilibrated mixture" means a mixture of MPOs in thermodynamic or kinetic equilibration.

As used herein, "fiber" means any material with elongated structure such as polymer or natural fibers. The material can be fiberglass, ceramic fibers, carbon fibers or organic polymers such as aramid fibers.

30 As used herein, a "tow" or "strand" means a group of fibers together, or a bundle of fibers, which are usually wound onto spools and may or may not be twisted. These tows or strands can be woven or knitted to form fabrics.

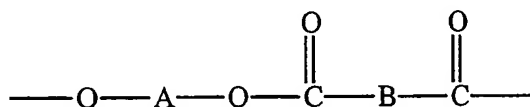
As used herein, a "fiber preform" means an assembly of fiber tows and/or fabric held together in a desired shape. Typically, fiber preforms are dry, and often held together with various tackifiers.

As used herein, a "prepreg" means a fiber material such as carbon fiber, glass fiber, or other fiber, that has been impregnated with a resin material in sufficient volume as to provide the matrix of the composite, and such that the ratio of fiber to resin is closely controlled. The fiber configuration can be in tow form, woven or knitted into a fabric, or in a unidirectional tape.

I. Macrocyclic Polyester Oligomers (MPOs)

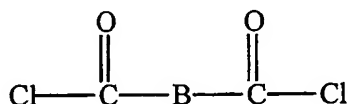
Many different MPOs can readily be made and are useful in the practice of this invention.

MPOs that may be employed in this invention include, but are not limited to, macrocyclic poly(alkylene dicarboxylate) oligomers having a structural repeat unit of the formula:



where A is an alkylene, or a cycloalkylene or a mono- or polyoxyalkylene group; and B is a divalent aromatic or alicyclic group. MPOs that may be employed in this invention may have various DP values, e.g., 2 to 20, 2 to 10, 2 to 8, and 2 to 6.

MPOs may be prepared by known methods. Synthesis of the preferred MPOs may include the step of contacting at least one diol of the formula HO-A-OH with at least one diacid chloride of the formula:



where A and B are as defined above. The reaction typically is conducted in the presence of at least one amine that has substantially no steric hindrance around the basic nitrogen atom. An illustrative example of such an amine is 1,4-diazabicyclo[2.2.2]octane (DABCO). The reaction usually is conducted under substantially anhydrous conditions in a substantially water immiscible organic solvent such as methylene chloride. The temperature of the reaction typically is between about -25°C and about 25°C. See, e.g., U.S. Patent No. 5,039,783 to Brunelle *et al.*

MPOs have also been prepared via the condensation of a diacid chloride with at least one bis(hydroxyalkyl) ester such as bis(4-hydroxybutyl) terephthalate. The condensation typically occurs in the presence of a highly unhindered amine or a mixture thereof with at least one other

tertiary amine such as triethylamine. Usually, a substantially inert organic solvent such as methylene chloride, chlorobenzene, or a mixture thereof is used. See, e.g., U.S. Patent No. 5,231,161 to Brunelle *et al.*

Another method for preparing MPOs, including macrocyclic co-polyester oligomers, is to depolymerize linear polyester polymers in the presence of an organotin or titanate compound. In this method, linear polyesters are converted to MPOs by heating a mixture of linear polyesters, an organic solvent, and a trans-esterification catalyst such as a tin or titanium compound. The solvents used, such as *o*-xylene and *o*-dichlorobenzene, usually are substantially free of oxygen and water. See, e.g., U.S. Patent Nos. 5,407,984 to Brunelle *et al.* and 5,668,186 to Brunelle *et al.*

It is also within the scope of the invention to employ macrocyclic homo- and co-polyester oligomers to produce homo- and co-polyester polymers, respectively. Therefore, unless otherwise stated, an embodiment of a composition, article, or process that refers to a MPO may also include co-polyester embodiments.

Among homopolymeric compositions and in one embodiment, MPOs of poly(1,4-butylene) terephthalate (PBT) are used. Among homopolymeric compositions and in another embodiment, MPOs of polyethylene terephthalate (PET) are used. Among co-polymeric compositions and in one embodiment, MPO species contain a major proportion of PBT structural units, PET structural units, or both. In one embodiment, MPO species contain at least about 90 mole percent of PBT structural units, PET structural units, or both. In another embodiment, MPO species contain predominately PBT, and a minor proportion of other units, for example, poly(alkylene dicarboxylate) units or ether oxygen-containing units such as those in which A is derived from diethylene glycol.

II. Designing Physical and Chemical Properties of MPO Compositions

In one embodiment, MPO compositions are created that have physical and/or chemical properties different from that of the unmodified MPO compositions originally produced. For example, the melting temperatures of a MPO composition can be significantly decreased by removal from the MPO composition of a major proportion of the macrocyclic polyester tetramer, i.e., the oligomer having a DP of 4. This is possible because the tetramer is both high melting and highly crystalline among the MPOs. Therefore, removal has a significant effect on the melting temperature and crystallinity of the oligomer composition. Similarly, the melting temperatures of a MPO composition can be significantly increased by adding into the MPO composition a significant proportion of the macrocyclic polyester tetramer.

In one aspect, the invention relates to a process for modifying a physical property of a composition having MPOs. The method includes the steps of (a) providing a composition having at least two species of MPOs, and (b) changing the weight percentage of at least one species of the MPOs in the composition. It should be understood that compositions may have three, four, 5 or five or more species of MPOs present. In addition, although preferably the weight percentage of one species of the MPOs in the composition is changed, the invention contemplates changing more than one species in a composition.

In one embodiment, the physical property to be modified is the melting temperature of the composition. Besides melting temperature, other physical properties that may be modified by the 10 method of the invention include, for example, crystallinity and viscosity. Modification of a selected physical property may be achieved by either increasing or reducing the weight percentage of at least one species of the MPOs in the composition.

In one embodiment, the weight percentage of at least the species having the highest melting temperature is reduced in step (b). In one embodiment, the weight percentage of at least 15 macrocyclic polyester tetramer is reduced in step (b). In one embodiment, the MPO composition includes macrocyclic PBT oligomers. In another embodiment, the MPO composition includes macrocyclic PET oligomers. The MPO composition may contain homo-oligomer, co-oligomer, or both. In one embodiment, a MPO composition includes a macrocyclic co-polyester oligomer that has at least about 90% mole percent PBT structural units.

20 The proportion of macrocyclic polyester tetramer present in products prepared by reactions under thermodynamic control is generally greater than the proportion resulting from reactions under kinetic control. An example of a thermodynamically controlled reaction is depolymerization. The reaction of a diol with a dicarboxylic acid chloride is chiefly kinetically controlled.

25 In one embodiment, the proportion of macrocyclic polyester tetramer removed according to the invention is at least 60% by weight of the total amount of the macrocyclic polyester tetramer in the oligomer composition as originally prepared. The amount of macrocyclic polyester tetramer present can vary according to the method of preparation of the oligomer composition. In another embodiment, at least 70% of the macrocyclic polyester tetramer is 30 removed. In yet another embodiment, at least 90% removal is performed.

In one embodiment, the reduction of the weight percentage of the macrocyclic polyester tetramer results in its weight percentage in the modified composition to be 60% less than its weight percentage in an equilibrated mixture of the MPOs according to the method of

preparation. In another embodiment, the weight percentage reduction is 70%. In yet another embodiment, the weight percentage reduction is 90%.

Any processes that result in modification of the weight percentage of a species of the MPOs may be employed. The effectiveness of such processes may be dependent on factors including the nature of the original MPO composition and the particular species the proportion of which is to be modified. Illustrative examples of such processes include distillation, fractional crystallization, anti-solvent precipitation, addition and mixing, chemical reactions, etc.

In one embodiment, removal of a species of MPOs is achieved by fractional crystallization. In one embodiment, the macrocyclic polyester tetramer is removed by fractional crystallization from a solution of the MPO composition. Any solvent that facilitates fractional crystallization may be employed. Illustrative suitable solvents include aromatic hydrocarbons and halogenated aromatic hydrocarbons, such as toluene, xylene and *o*-dichlorobenzene (ODCB). For example, in one embodiment, a 5% by weight solution of oligomer composition in ODCB at 110°C is cooled to ambient temperature of about 25°C, whereupon a precipitate forms that contains a major proportion of the tetramer.

In one embodiment, removal of the macrocyclic polyester tetramer is achieved by anti-solvent precipitation. Illustrative suitable non-solvents include aliphatic hydrocarbons, especially those in the C₆₋₁₀ range such as hexane, heptane, octane and decane. In one preferred embodiment, heptane is used.

In one embodiment of a process of removing macrocyclic polyester tetramer by anti-solvent precipitation, the non-solvent is added to the MPO solution at an elevated temperature, in the range of about 80-120°C, after which the mixture is allowed to cool to a lower temperature, typically no higher than about 70°C since at lower temperatures substantial amounts of other oligomers, or the MPO composition in its entirety, may be precipitated. The amount of non-solvent added is most often about 90-110% by volume of solvent used. Upon cooling to this lower temperature, a precipitate forms that is predominantly the macrocyclic polyester tetramer. A minor proportion of the macrocyclic polyester tetramer originally present usually remains in the MPO composition in solution. However, the remaining macrocyclic polyester tetramer does not have a significant effect on the melting temperature and crystallinity of the MPO composition.

The MPO species removed may be reused for various purposes. In one embodiment, the MPO species, e.g., macrocyclic polyester tetramer, is polymerized separately or in combination with other MPOs or linears to produce linear polyester. In another embodiment, the MPO

species is equilibrated with linear polyester that is intended to be depolymerized, either before or during the depolymerization reaction. Depolymerization of a mixture of linear polyester and the MPO species removed from a MPO composition provides an oligomeric product that has the same distribution of oligomers as that obtained from linear polyester alone, showing that

5 equilibration is essentially complete.

The apparatus for performing the above modification processes may be any conventional apparatus. The actual apparatus will depend on the actual process being employed. In one embodiment for performing fractional crystallization (referring to FIG. 1), an apparatus for producing the compositions of the invention may include a reactor vessel 110 in which the
10 reaction constituents 120, e.g., linear polyester, solvent and depolymerization catalyst, are combined and the depolymerization reaction conducted. Subsequently, the product mixture passes through a filter 130 to remove linears. The filtrate may pass into a second vessel 140 where it is cooled to room temperature either in the presence or absence of aliphatic hydrocarbon as non-solvent to precipitate a species of MPO, e.g., the tetrameric species. The filtrate is then
15 passed through another filter 150 which removes the precipitate, e.g., macrocyclic polyester tetramer. The precipitated macrocyclic polyester oligomers can be removed from the filter 150 and recycled to the reactor vessel 110. Further vessels may be employed downstream to isolate the product in the desired form and to remove non-solvent when it is employed.

In a preferred embodiment of the invention, a MPO composition includes at least two
20 species of MPOs wherein the species having the highest melting temperature is present in an amount less than or equal to 10%, preferably less than or equal to 5%, more preferably less than or equal to 3%.

In one embodiment, the MPOs in the MPO composition have a DP from 2 to about 20. In another embodiment, the MPOs have a DP from 2 to about 10. In another embodiment, the
25 MPOs have a DP from 2 to about 8. In yet another embodiment, the MPOs have a DP from 2 to about 6.

In one embodiment, the species having the highest melting temperature is macrocyclic polyester tetramer. In one embodiment, the MPO composition includes macrocyclic PBT oligomers. In another embodiment, the MPO composition includes macrocyclic PET oligomers.
30 The MPO composition may contain homo-oligomer, co-oligomer, or both. In one embodiment, the MPO composition includes a macrocyclic co-polyester oligomer that has at least about 90% mole percent PBT structural units.

In one embodiment, the MPO composition includes 30-40% macrocyclic polyester dimers, 30-45% macrocyclic polyester trimers, 0-5% macrocyclic polyester tetramers, and 5-20% macrocyclic polyester pentamers. In some embodiments, the percentage of macrocyclic polyester tetramers preferably is less than about 3%, more preferably less than about 2%, or most

5 preferably less than about 1%.

In one embodiment, the MPO composition includes a filler. In another embodiment, the MPO composition includes a polymerization catalyst. In another embodiment, the MPO composition is part of a prepreg composition.

MPO compositions in which a major proportion of the macrocyclic polyester tetramer has
10 been removed have melting temperatures significantly lower than those of corresponding compositions containing macrocyclic polyester tetramer in the original proportions, i.e., the unmodified product mixtures (equilibrated or nearly equilibrated) of the MPO-forming reactions. The melting temperatures typically are wide ranges by reason of the various kinds of MPO molecules in the MPO compositions. The most pronounced decrease in temperature is in the
15 upper value of the range, i.e., the temperature at which the last trace of solid melts. Typically, the upper value of the melting temperature range of a modified MPO composition may be from about 15°C to as much as 70°C lower than the upper value for the unmodified original MPO composition.

This decrease in melting temperature is typically accompanied by a significant decrease in
20 crystallinity, particularly upon heating above the melting temperature followed by quenching. Thus, MPO compositions in which macrocyclic polyester tetramer has been removed can be quenched and used to impregnate fibrous or other fillers, whereupon a prepreg composition capable of being draped and shaped is produced.

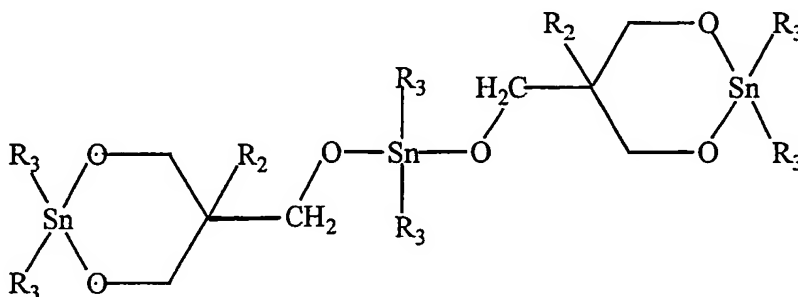
III. Polymerization catalysts

25 Polymerization catalysts that may be employed in the invention are capable of catalyzing the polymerization of MPOs. Organotin and organotitanate compounds are preferred catalysts, although other catalysts may be used. For example, organotin compound 1,1,6,6-tetra-n-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane may be used as polymerization catalyst. Other illustrative organotin compounds include n-butyltin(IV) chloride dihydroxide, dialkyltin(IV)
30 oxides, such as di-n-butyltin(IV) oxide and di-n-octyltin oxide, and acyclic and cyclic monoalkyltin (IV) derivatives such as n-butyltin tri-n-butoxide, dialkyltin(IV) dialkoxides such as di-n-butyltin(IV) di-n-butoxide and 2,2-di-n-butyl-2-stanna-1,3-dioxacycloheptane, and

trialkyltin alkoxides such as tributyltin ethoxide. See, e.g., U.S. Patent No. 5,348,985 to Pearce *et al.*

Also, trisstannoxanes having the general formula (I) shown below can be used as a polymerization catalyst to produce branched polyester polymers.

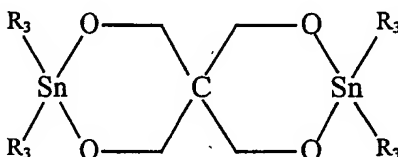
(I)



where R_2 is a C_{1-4} primary alkyl group and R_3 is C_{1-10} alkyl group.

Additionally, organotin compounds with the general formula (II) shown below can be used as a polymerization catalyst to prepare branched polyester polymers from MPOs.

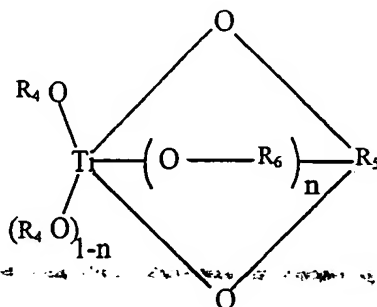
(II)



where R_3 is defined as above.

As for titanate compounds, tetra(2-ethylhexyl) titanate, tetraisopropyl titanate, tetrabutyl titanate, and titanate compounds with the general formula (III) shown below can be used as polymerization catalysts.

(III)



wherein: each R_4 is independently an alkyl group, or the two R_4 groups taken together form a divalent aliphatic hydrocarbon group; R_5 is a C_{2-10} divalent or trivalent aliphatic hydrocarbon group; R_6 is a methylene or ethylene group; and n is 0 or 1.

Typical examples of titanate compounds with the above general formula are shown in

5 Table 1.

Table 1. Examples of Titanate Compounds Having Formula (III)

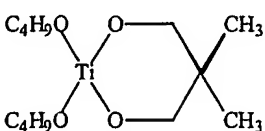
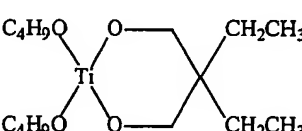
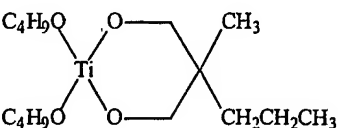
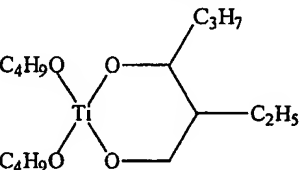
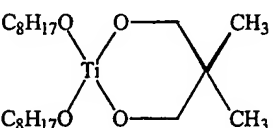
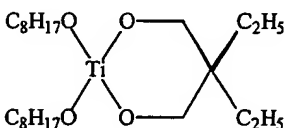
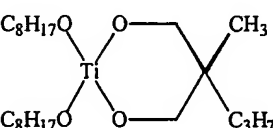
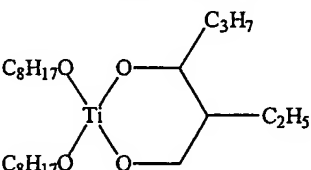
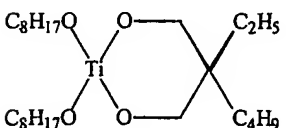
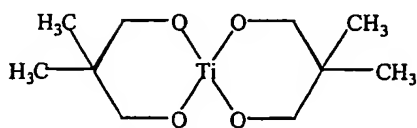
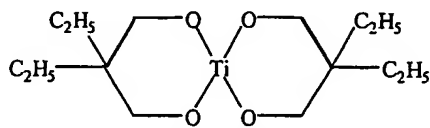
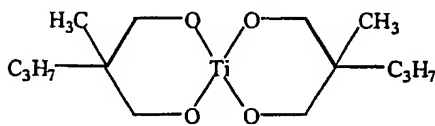
 <p>Di-1-butyl 2,2-dimethylpropane-1,3-dioxytitanate</p>	 <p>Di-1-butyl 2,2-diethylpropane-1,3-dioxytitanate</p>
 <p>Di-1-butyl 2-(1-propyl)-2-methylpropane-1,3-dioxytitanate</p>	 <p>Di-1-butyl 2-ethylhexane-1,3-dioxytitanate</p>
 <p>Di(2-ethyl-1-hexyl) 2,2-dimethylpropane-1,3-dioxytitanate</p>	 <p>Di(2-ethyl-1-hexyl) 2,2-diethylpropane-1,3-dioxytitanate</p>
 <p>Di(2-ethyl-1-hexyl) 2-(1-propyl)-2-methylpropane-1,3-dioxytitanate</p>	 <p>Di(2-ethyl-1-hexyl) 2-ethylhexane-1,3-dioxytitanate</p>
 <p>Di(2-ethyl-1-hexyl) 2-(1-butyl)-2-ethylpropane-1,3-dioxytitanate</p>	

Table 1. Examples of Titanate Compounds Having Formula (III) (Cont'd)

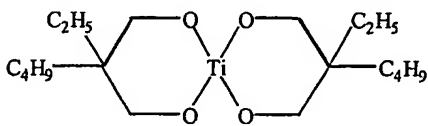
Bis(2,2-dimethyl-1,3-propylene) titanate



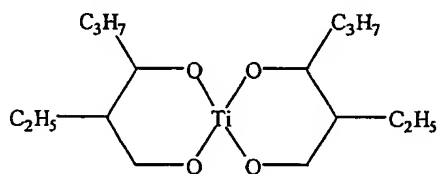
Bis(2,2-diethyl-1,3-propylene) titanate



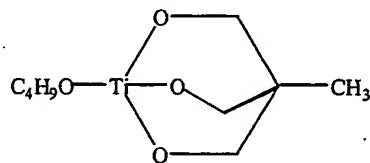
Bis(2-(1-propyl)-2-methyl-1,3-propylene) titanate



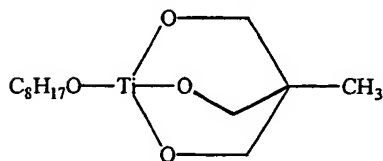
Bis(2-(1-butyl)-2-ethyl-1,3-propylene) titanate



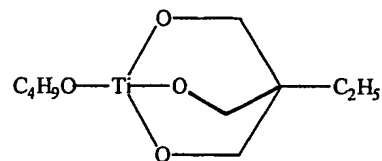
Bis(2-ethyl-1,3-hexylene) titanate



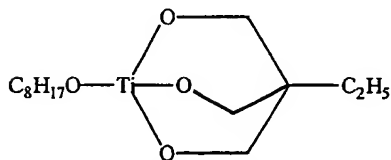
1-(1-Butoxy)-4-methyl-2,6,7-trioxabicyclo[2,2,2]octane



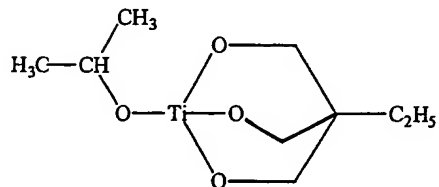
1-(2-ethyl-1-hexoxy)-4-methyl-2,6,7-trioxabicyclo[2,2,2]octane



1-(1-Butoxy)-4-ethyl-2,6,7-trioxabicyclo[2,2,2]octane



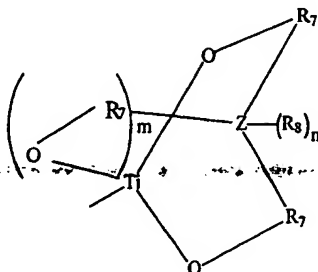
1-(2-ethyl-1-hexoxy)-4-ethyl-2,6,7-trioxabicyclo[2,2,2]octane



1-(2-Propoxy)-4-ethyl-2,6,7-trioxabicyclo[2,2,2]octane

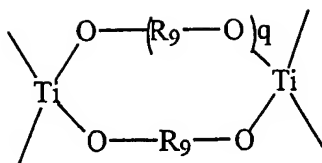
- 5 Titanate ester compounds having at least one moiety of the following general formula have also been used as polymerization catalysts:

(IV)



or

(V)



wherein:

each R_7 is independently a C_{2-3} alkylene group;

5 R_8 is a C_{1-6} alkyl group or unsubstituted or substituted phenyl group;

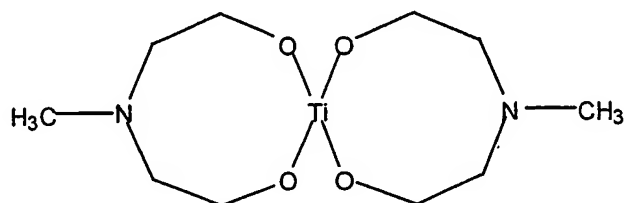
Z is O or N; provided when Z is O, $m = n = 0$, and when Z is N, $m = 0$ or 1 and $m + n = 1$;

each R_9 is independently a C_{2-6} alkylene group; and q is 0 or 1.

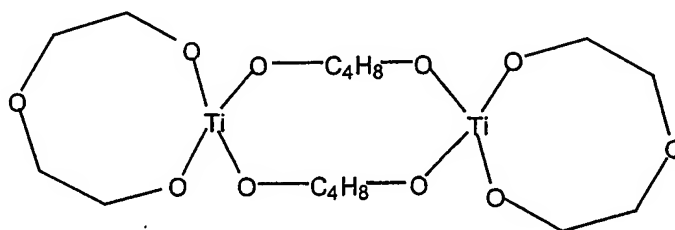
Typical examples of such titanate compounds are shown below as formula (VI) and formula (VII):

10

(VI)



(VII)



IV. The Blend Material

A blend material comprising MPOs and a polymerization catalyst allows for easy
 15 production, storage, transportation and processing. From the standpoint of applications, the
 blend material is a one-component ready-to-use mixture. The blend material may also be
 processed like a thermoset while producing a thermoplastic. Furthermore, the blend material
 may eliminate the need for existing equipment to be modified to allow for transfer of the MPO
 and a polymerization catalyst into the equipment in the appropriate amounts at the appropriate
 20 time and at the appropriate temperature.

In one aspect, the invention relates to a blend material comprising a MPO composition with a modified physical property (e.g., the melting temperature as described above) and a polymerization catalyst.

There is no limitation with respect to the physical form of the MPO when mixed with the polymerization catalyst as long as the MPO remains substantially chemically intact. In one embodiment, the MPO is a solid such as a powder. In this embodiment, mechanical mixing typically is used to mix MPO with a polymerization catalyst. In another embodiment, the MPO is mixed in the presence of a solvent with the solvent remaining present during the step of mixing.

In one embodiment, the blend material also includes a filler as described above. Illustrative examples of such fillers include pigments, light weight fillers, flame retardants, and ultraviolet light stabilizers. For example, calcium carbonate may be used to increase the thickness of a polyester polymer product to improve its mechanical performance. Also, glass microspheres may be added to lower the density of the product. Other fillers include nanoclays, e.g., to increase the modulus of the product, organo bromides in combination with antimony oxides, e.g., to impart flame resistance, and colorants such as carbon black or titanium dioxide.

The filler is added generally between about 0.1% and 70% by weight, between about 25% and 70% by weight, or between about 2% and 5% by weight depending on the filler and the purpose for adding the filler. For example, the percentage is preferably between 25% and 50% by weight in the case of calcium carbonate, between 2% and 5% by weight in the case of nanoclays, between 0.1% and 1% in the case of pigments, and between 25% and 70% by weight in the case of glass microspheres.

A process for preparing the blend material includes providing a MPO and mixing the MPO with a polymerization catalyst. When preparing the blend, the MPO and the polymerization catalyst may be mixed together by various means. For example, any conventional mixer or blender may be employed to mix the MPO with the polymerization catalyst via agitation at temperatures below the melting temperature of the MPO. This process may be conducted under an inert atmosphere such as a nitrogen atmosphere.

A solvent may also be employed to assist in the uniform mixing of the MPO with the polymerization catalyst. Various solvents can be used, and there is no limitation with respect to the type of solvent that may be used other than that the solvent is substantially free of water.

Illustrative examples of solvents that may be employed in the invention include methanol,

ethanol, isopropanol, acetone, methyl ethyl ketone, benzene, toluene, *o*-xylene, chlorobenzene, dichloromethane, and chloroform.

There is no limitation with respect to the amount of solvent to be employed other than that the amount results in a uniform mixing of the MPO and the polymerization catalyst. In one embodiment, the blend of MPO with the polymerization catalyst is isolated either by direct removal of the solvent via evaporation or by precipitation via addition of the mixture into a nonsolvent. In another embodiment, the blend of solid ingredients is further dried under vacuum at elevated temperatures below the melting temperature of the MPO to remove any residual solvent.

A process for preparing the blend material further having at least one filler, or any other additional material, is generally the same as described above, however, the characteristics of the filler and/or additional materials must be considered. It should be understood that the MPO, the polymerization catalyst, the filler, any additional material(s) and/or solvent, if used, may be mixed in any order or simultaneously as long as the final composition contains the appropriate amount of each ingredient.

It is within the scope of the invention to employ one, two or more different fillers in preparing a blend material of MPO and polymerization catalyst. Unless specifically stated otherwise, any embodiment of a composition, article or process that refers to filler in singular also includes an embodiment wherein two or more different fillers are employed. Similarly, unless stated otherwise, any embodiment of a composition, article or process that refers to fillers in plural also includes an embodiment wherein one filler is employed.

In one embodiment of the invention, the amount of polymerization catalyst employed is generally about 0.01 to about 10.0 mole percent, preferably about 0.1 to about 2 mole percent, and more preferably about 0.2 to about 0.6 mole percent based on total moles of monomer repeat units of the MPO.

Although dependent on the particular composition of the blend material, blend materials typically exhibit a shelf life generally longer than a week, and preferably longer than a month, and more preferably longer than a year when stored at ambient temperature.

It is within the scope of the invention to employ one, two or more different polymerization catalysts in preparing a blend of MPO and polymerization catalyst. Unless specifically stated otherwise, any embodiment of a composition, article or process that refers to polymerization catalyst in singular also includes an embodiment wherein two or more different polymerization catalysts are employed. Similarly, unless stated otherwise, any embodiment of a

composition, article or process that refers to polymerization catalyst in plural also includes an embodiment wherein one polymerization catalyst is employed. Two or more polymerization catalysts may be used to vary the rate of polymerization and to produce polyesters with variable degrees of branching.

5 **V. Polymerization of MPOs**

10 In another aspect, the invention relates to a process for polymerizing a MPO composition that includes the steps of (a) providing a MPO composition with a modified physical property (e.g., the melting temperature as described above), (b) providing a polymerization catalyst, and (c) polymerizing the MPOs. The MPOs and the polymerization catalyst may be components of a blend material. Therefore, in one embodiment, a process for polymerizing a MPO composition includes the steps of (a) providing a blend material having a MPO composition with a modified physical property, e.g., the melting temperature, and (b) polymerizing the MPOs. In one embodiment, the polymerization is conducted in the range of 130 °C to 230 °C.

15 By reason of the lower melting temperature and decrease in crystallinity, it is frequently possible to polymerize the compositions of the present invention to linear polyesters at lower temperatures than with previously known MPO compositions. For example, a conventionally prepared macrocyclic PBT oligomer composition may require a polymerization temperature (in the presence of a conventional tin compound as catalyst) on the order of 190°C and will not polymerize at 150°C. The corresponding composition, from which most of the tetramer has been
20 removed according to this invention, has been polymerized to high molecular weight PBT at temperatures as low as 148°C.

25 In other respects, the compositions of MPOs in which tetramers have been removed are similar to known MPO compositions in that they may be polymerized under a wide variety of conditions in the presence of polymerization catalysts to linear polyesters having a wide variety of uses.

30 Blends of MPOs with catalyst and/or filler may be polymerized in processes such as rotational molding, resin film infusion, pultrusion, resin transfer molding, filament winding, making and using powder-coated or hot melt prepreg, water slurry process, compression molding, and roll wrapping. These processes may be used to form polyester compositions, including composites, which may be included in articles of manufacture such as carbon fiber golf shafts and lightweight automotive chassis members, construction materials, and so on.

The following examples are provided to further illustrate and to facilitate the understanding of the invention. These specific examples are intended to be illustrative of the invention.

Example A General Depolymerization Procedure

5 Dissolve dry poly(1,4-butylene terephthalate) (PBT) pellets in dry *o*-dichlorobenzene (ODCB) under inert atmosphere at 180°C. Add a titanate catalyst as a solution in ODCB or as a neat solid. The depolymerization reaction is carried out at about 180°C. The reaction can be sampled over time to determine progress. When equilibrium is reached (usually within 1 hour), the reaction is cooled to 100°C and water is added to quench the titanate catalyst
10 (add about 0.5% water by volume). After quenching, the reaction mixture is concentrated by removing 70-95% of the ODCB. This step can be done from 70-180°C by adjusting pressure during the strip.

After the initial concentration step, the reaction is allowed to cool to about 70°C and filtered to remove the bulk of the linears which fall from solution. The filtrate, which contains
15 the MPOs, is concentrated to about 30% solids at about 110°C. An equal volume of heptane is added and the reaction is allowed to cool to about 70°C to precipitate the PBT tetramer. Filter to remove the PBT tetramer and pass the filtrate through a column of alumina to remove residual linears. Pure MPOs are then isolated by heptane precipitation or by concentration.

PBT used in these experiments was produced by General Electric (Valox 315 grade) and
20 was dried in *vacuo* at about 120°C before use. Anhydrous ODCB was used as received from Aldrich. Titanate catalysts were prepared from tetrakisopropyl titanate from DuPont that was vacuum distilled prior to use. Diols that were dried over molecular sieves. All other reagent grade solvents and chemicals were used as received.

HPLC analysis was used to characterize the composition of the MPOs and to follow
25 progression of depolymerization reactions. HPLC analysis was conducted using a Hewlett Packard Series 1050 chromatography system. Samples were eluted at 1.5 ml/min through a 4.6 x 15 cm Zorbax Eclipse XBD-C8 column at 40°C. A linear acetonitrile:water gradient which ramped from 50:05 to 100:0 over 18 min was used. Analysis was calibrated using pure PBT dimer which was isolated by vacuum sublimation. MPOs were quantified using phenanthrene as
30 an internal calibration standard. Peaks were measured at 254 nm with a UV detector.

Analyses for polymer M_w were conducted using a Hewlett Packard Series 1100 chromatography system. Samples were eluted at 1 ml/min with chloroform through a bank of

two Phenomenex Phenogel 5 μ m linear 300 x 7.8 mm columns at 40°C. Peaks were detected with a UV detector at 254 nm and the instrument was calibrated using polystyrene standards.

HPLC retention times of MPOs are shown in Table 1. Melting range data of select MPO compositions is shown in Table 2.

5

Table 1. HPLC Retention Times of Select MPOs

MPO	Dimer (PBT)	Trimer (PBT)	Tetramer (PBT)	Pentamer (PBT)
HPLC T _r (min.)	6.8	11.5	13.6	15.4

Table 2. Melting Ranges of Select MPO Compositions

Sample	%Dimer	%Trimer	%Tetramer	%Pentamer	% co-MPO	Melt Range °C
a	13.1	12.9	51.9	11.7	9.3	175-218
b	2	46.7	29.8	21.5	0	120-215
c	32.2	38.2	16.6	13.1	0	120-200
d	34.5	29.9	12.8	11.2	13.8	125-175
e	30.6	34.3	10.2	10.2	14.2	125-168
f	37.1	37	1.48	10	14.5	125-148

10 *Example 1*

A 22.2 g sample of commercially available PBT was dissolved in 1,450 g (1,107 ml) of ODCB and depolymerized in the presence of 2.8 mole percent of a mixed 1,4-butanediol/2-methyl-2,4-pentanediol (4.3:1 molar) titanate catalyst. MPOs were obtained in the amount of 11.4 g, or 51.8% of theoretical.

15 The reaction mixture was quenched with water at 100°C and ODCB was distilled off to a MPO concentration of 11% by weight (71 ml of ODCB). A sample was removed and stripped of solvent; it was found to have a melting temperature of 100-210°C.

Heptane, 71 ml, was added to the remaining oligomer composition at 110°C and the reaction mixture was allowed to cool to 70°C, whereupon a precipitate formed. The mixture was
20 filtered; the filtration residue was found by HPLC analysis to contain about 96% by weight of the tetramer in the reaction product. The filtrate was poured into an excess of heptane to precipitate the remaining oligomers which were found to have a melting temperature of 100-150°C.

Example 2

A 250 ml round-bottomed flask equipped with a magnetic stirrer was charged with 85 g
25 (64 ml) of ODCB and 15 g of a macrocyclic PBT oligomer composition prepared by the reaction

of terephthaloyl chloride with bis(4-hydroxybutyl) terephthalate. A control sample of the oligomer composition was found to have a melting temperature of 100-180°C.

Heptane, 64 ml, was added slowly to the remaining oligomer composition at 110°C and the reaction mixture was allowed to cool over 1 hour to 75°C, whereupon a precipitate formed.

- 5 The mixture was filtered; the filtration residue was found to contain about 90% by weight of the cyclic tetramer in the reaction product. The filtrate was poured into an excess of heptane to precipitate the remaining oligomers which were found to have a melting temperature of 100-130°C.

Example 3

- 10 A 3 l round-bottomed flask equipped with a magnetic stirrer and thermometer was charged with 700 g (534 ml) of ODCB and 300 g of a macrocyclic PBT oligomer composition prepared by the reaction of terephthaloyl chloride with 1,4-butanediol. A control sample of the oligomer composition was found to have a melting temperature of 120-175°C.

- 15 The mixture was heated to 110°C to dissolve all of the oligomers and heptane, 534 ml, was added slowly at 110°C. The reaction mixture was allowed to cool to 75°C, whereupon a precipitate formed. The mixture was filtered; the filtration residue was found to contain about 73% by weight of the cyclic tetramer in the reaction product. The filtrate was poured into an excess of heptane to precipitate the remaining oligomers which were found to have a melting temperature of 120-158°C.

20 Example 4

- A 5% (by weight) solution in ODCB of macrocyclic PBT oligomers, prepared as described in Example 1, was found to be a homogeneous liquid at 110°C. Upon cooling to room temperature, a precipitate deposited from the solution. The precipitate was found by analysis to be 90% pure cyclic tetramer, and to constitute 60% by weight of the tetramer present in the
25 original oligomer composition.

Example 5

- A 300 mg control sample of the PBT oligomer composition employed in Example 2, from which the tetramer had not been removed, was placed in a test tube and submerged in an oil bath maintained at 150°C for 10 minutes. The composition did not melt at this temperature. A
30 sample of the product of Example 2, from which tetramer had been removed, melted when heated to the same temperature but crystallized to an opaque, brittle solid upon cooling.

When the product of Example 2 was heated to 150°C and quenched by submersion in cold water, it remained transparent, indicating that it was amorphous rather than crystalline after quenching. It remained amorphous and tacky after storing at ambient temperature for one month. By contrast, the control returned to a brittle, crystalline state upon standing for 48 hours.

5 **Example 6**

A 3 l round-bottomed flask was charged with 3,098 ml of ODCB, 26.3 g of commercially available PBT pellets, and 4.9 g of tetramer removed from a MPO composition as described in Example 3. The resulting mixture was heated to 180°C until all solids were dissolved and a titanate catalyst similar to that of Example 1 was added in a similar proportion to PBT. Heating
10 at 180°C was continued for one hour, after which a portion of the mixture was analyzed and found to contain MPOs in a proportion similar to that observed in Example 1.

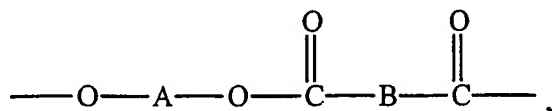
While typical embodiments have been set forth for the purpose of illustration, the foregoing descriptions and examples should not be deemed to be a limitation on the scope of the invention. Accordingly, various modifications, adaptations, and alternatives may occur to one
15 skilled in the art without departing from the spirit and scope of the present invention.

The patents and references referred to above are incorporated by reference including:
U.S. Patent Nos. 5,039,783, 5,191,013, 5,231,161, 5,348,985, 5,389,719, 5,407,984, 5,466,744,
5,591,800, 5,661,214, 5,668,186, and 5,710,086.

What is claimed is:

1. A process for modifying a physical property of a composition comprising macrocyclic polyester oligomers, comprising the steps of:

(a) providing a composition comprising at least two species of macrocyclic polyester oligomers, each of said macrocyclic polyester oligomers comprising a structural repeat unit of the formula



wherein

A is an alkylene, a cycloalkylene, or a mono- or polyoxyalkylene group, and

B is a divalent aromatic or alicyclic group; and

(b) changing the weight percentage of at least one species of said macrocyclic polyester oligomers in said composition.

2. The process of claim 1 wherein said physical property is the melting temperature of said composition.

3. The process of claim 1 wherein said at least one species of said macrocyclic polyester oligomers in step (b) is the highest melting temperature macrocyclic polyester oligomer in said composition.

4. The process of claim 1 wherein said at least one species of said macrocyclic polyester oligomers in step (b) comprises at least said macrocyclic polyester tetramer.

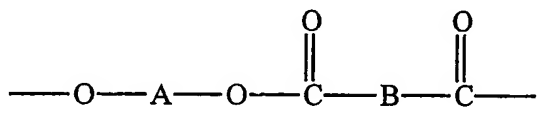
5. The process of claim 4 wherein step (b) comprises reducing the weight percentage of at least the macrocyclic polyester tetramer.

6. The process of claim 1 wherein said at least two species of macrocyclic polyester oligomers in step (a) have a degree of polymerization from 2 to 10.

7. The process of claim 6 wherein said at least two species of macrocyclic polyester oligomers in step (a) have a degree of polymerization from 2 to 6.

8. The process of claim 1 wherein said composition comprises macrocyclic poly(1,4-butylene terephthalate) oligomers.

- 1 9. The process of claim 1 wherein said composition comprises macrocyclic poly(ethylene
2 terephthalate) oligomers
- 1 10. The process of claim 1 wherein said composition comprises a macrocyclic copolyester
2 oligomer
- 1 11. The process of claim 10 wherein said composition comprises a macrocyclic copolyester
2 oligomer containing at least about 90 mole percent poly(1,4-butylene terephthalate)
3 structural units.
- 1 12. The process of claim 1 wherein step (b) comprises performing fractional crystallization.
- 1 13. A macrocyclic polyester oligomer composition having a decreased melting temperature
2 produced by the process of claim 1.
- 1 14. A macrocyclic polyester oligomer composition comprising at least two species of
2 macrocyclic polyester oligomers, each of said macrocyclic polyester oligomers
3 comprising a structural repeat unit of the formula

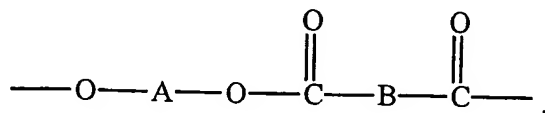


- 4
5 wherein
6 A is an alkylene, a cycloalkylene or a mono- or polyoxyalkylene group, and
7 B is a divalent aromatic or alicyclic group,
8 wherein a species of said macrocyclic polyester oligomers having the highest melting
9 temperature is present in an amount less than or equal to 5%.
- 1 15. The composition of claim 14 wherein each of said macrocyclic polyester oligomers has a
2 degree of polymerization in the range from 2 to about 6.
- 1 16. The composition of claim 15 wherein said species having the highest melting temperature
2 is macrocyclic polyester tetramer.
- 1 17. The composition of claim 14 wherein said macrocyclic polyester oligomers comprise
2 macrocyclic poly(1,4-butylene terephthalate) oligomers.

- 1 18. The composition of claim 14 wherein said macrocyclic polyester oligomers comprise
2 macrocyclic poly(ethylene terephthalate) oligomers.
- 1 19. The composition of claim 15 wherein said macrocyclic polyester oligomers comprise a
2 macrocyclic copolyester oligomer comprising at least about 90 mole percent poly(1,4-
3 butylene terephthalate) structural units.
- 1 20. The composition of claim 14 further comprising a filler.
- 1 21. The composition of claim 14 further comprising a polymerization catalyst.
- 1 22. A prepreg composition comprising the composition of claim 14.
- 1 23. A blend material comprising:
2 (a) the macrocyclic polyester oligomer composition of claim 14; and
3 (b) a polymerization catalyst.
- 1 24. The blend material of claim 23 further comprising a filler.
- 1 25. The blend material of claim 24 wherein said filler is present at a weight
2 percentage of from 0.1% to 70%.
- 1 26. A polyester polymer composite prepared by polymerizing said macrocyclic
2 polyester oligomers of said blend material of claim 23.
- 1 27. An article of manufacture comprising said polyester polymer composite of claim
2 26.
- 1 28. A process for polymerizing a macrocyclic polyester oligomer composition
2 comprising the steps of:
3 (a) providing the macrocyclic polyester oligomer composition of claim 14;
4 (b) providing a polymerization catalyst; and
5 (c) polymerizing said macrocyclic polyester oligomers.
- 1 29. A process for polymerizing a macrocyclic polyester oligomer composition
2 comprising the steps of:
3 (a) providing the blend material of claim 23; and
4 (b) polymerizing said macrocyclic polyester oligomers.

- 1 30. The process of claim 29 wherein step (b) is conducted at a temperature between
2 130°C and 230°C.

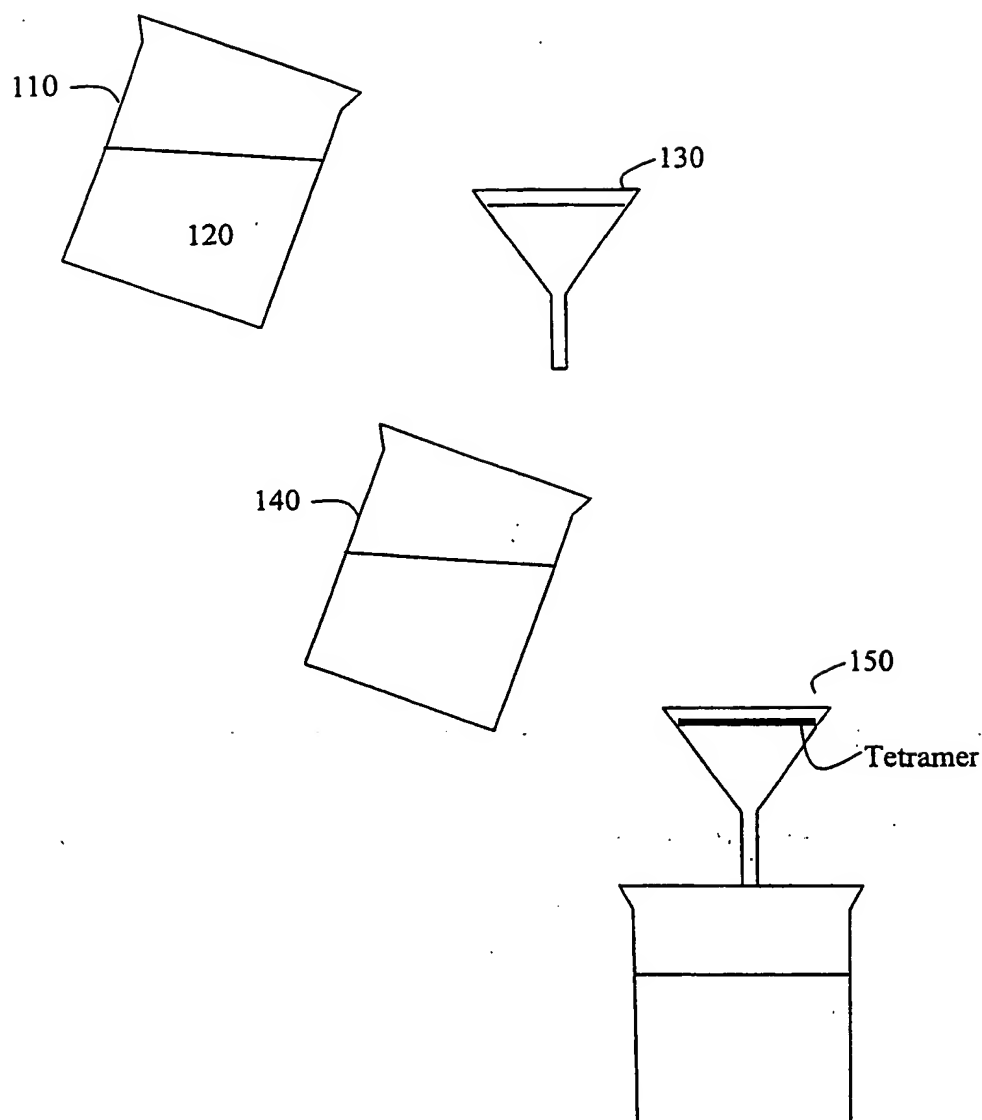
- 1 31. A macrocyclic polyester oligomer composition comprising 30-40% macrocyclic polyester
2 dimers, 30-45% macrocyclic polyester trimers, 0-5% macrocyclic polyester tetramers, and
3 5-20% macrocyclic polyester pentamers, each of said macrocyclic polyester oligomers
4 comprising a structural repeat unit of the formula



6 wherein

7 A is an alkylene, a cycloalkylene or a mono- or polyoxyalkylene group, and
8 B is a divalent aromatic or alicyclic group.

- 1 32. The composition of claim 31 wherein said macrocyclic polyester oligomer composition
2 comprises less than 3% of macrocyclic polyester tetramers.

**Fig. 1**

INTERNATIONAL SEARCH REPORT

Inter Application No

PCT/US 01/27648

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L67/02 C08G63/78 //(C08L67/02,67:02)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 601 753 A (GEN ELECTRIC) 15 June 1994 (1994-06-15) claims 1-13	1-11, 13-32 12
Y	GB 1 108 921 A (DU PONT) 10 April 1968 (1968-04-10) page 5, line 1 - line 12	12
X	US 5 191 013 A (COOK TODD D ET AL) 2 March 1993 (1993-03-02) cited in the application claims 1,2; example 26	1-32

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

18 March 2002

Date of mailing of the international search report

27/03/2002

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/27648

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